

# **FY 2002 ANNUAL OPERATING PLAN**

## **HYDROGEN PROGRAM**

*Prepared for*

**U. S. DEPARTMENT OF ENERGY  
OFFICE OF POWER TECHNOLOGIES**

*by*

**ENERGETICS, INCORPORATED**

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## 1.0 INTRODUCTION

This document is the Annual Operating Plan of the Department of Energy (DOE), Hydrogen Research and Development (R&D) Program. It serves to provide the DOE's management and program participants with the plans for fiscal year 2002 (FY 2002). This document contains general information on the Hydrogen R&D Program and its goals, project summaries listing the planned activities for FY 2002 (including Gantt charts with expected critical and key milestones), significant results and accomplishments from 2001, and listings of publications, patents, and national recognition achieved by the Principal Investigators.

The Hydrogen Program is part of the Office of Hydrogen and Superconductivity within the Office of Power Technologies (OPT), which is in turn within the Office of Energy Efficiency and Renewable Energy. The organization of the Hydrogen Program is detailed in Chapter 2. The Program includes three focus areas: A) Research and Development of Critical Component Technologies (production, storage, and utilization), B) Technology Validation, and C) Analysis and Outreach.

The DOE Hydrogen R&D Program is responsive to the National Energy Policy (NEP) report of 2001 and has historically supported the Matsunaga Hydrogen Research, Development, and Demonstration Act of 1990 (P.L. 101-566), the Energy Policy Act of 1992 (P.L. 102-486) Section 2026, and the Hydrogen Future Act of 1996 (P.L. 104-271), and addresses the energy and environmental benefits of hydrogen. The Program put forth by the DOE, in collaboration with industry and other Federal entities, has been designed to develop the technologies necessary to safely produce, store, transport, and utilize hydrogen as an energy carrier; to illustrate the energy and environmental benefits to the public sector; and to initiate the transition strategy which can bring these technologies successfully to the marketplace.

### 1.1 Supporting the National Energy Policy Report

The recent release of the NEP has validated the role of the Hydrogen Program as it recommends the development of projects similar in scope to those that the Hydrogen Program has been funding for several years. For example, the NEP calls for utilizing R&D advances by supporting the Department of Transportation fuel cell transit bus program, DOE's Hydrogen program has been developing small-scale reformers and advanced electrolyzers for bus refueling for 5 years. In the near term, fuel cell vehicles will most likely be used in fleet applications to accommodate higher vehicle costs as well as fueling, operation, and maintenance requirements. Hydrogen-fueled buses will also be utilized in a few urban areas and also by some progressive transit agencies that have compressed natural gas (CNG) fueling facilities. DOE's overall mission is to replace 30% of petroleum-based motor fuels by the year 2010. Additionally, the NEP raises the issue of issuing a tax credit for hybrid or fuel cell vehicles; DOE has been funding programs that field-validate distributed fueling stations. This supports hydrogen infrastructure options for hybrid or fuel cell vehicles.

The NEP specifically recognizes hydrogen as a valid future source of energy and has made recommendations to advance R&D, step up the education campaign, integrate hydrogen, fuel cells and distributed energy resources (DER), and support upcoming Future Act legislation. DOE's Hydrogen program has historically funded, and continues to fund the development of natural gas-to-hydrogen reformers, biomass and coal to hydrogen systems, reversible fuel cells and electrolyzers, as well as high pressure and adsorbent storage systems. In addition, the Program is producing a joint education film with Worldwatch on hydrogen energy and continues to support codes and standards activities. The program conducts field verification activities on power-park concepts, including the use of hydrogen fuel cells and storage systems as well as automotive fuel cells for electric generation. The Hydrogen program continues to provide testimony for hydrogen legislation.

## 1.2 Implementing the Twenty-Year Vision

Hydrogen allows for both the increased use of renewable energy and CO<sub>2</sub> sequestration technologies that help to reduce CO<sub>2</sub> emissions. It can replace conventional fuels and result in near-zero urban pollutants being emitted into the atmosphere. With this in mind, the DOE Hydrogen program laid out its Twenty-Year Vision in the Strategic Plan:

**In the next twenty years, concerns about global climate change and energy security will create the platform for the penetration of hydrogen into several niche markets. Ultimately, hydrogen and electricity will come from sustainable renewable energy resources, but fossil fuels will be a significant transitional resource during this period. The growth of fuel cell technology will provide a base for the establishment of the hydrogen option into both transportation and electricity supply markets.**

Since the strategic plan was written in 1998, the Hydrogen Program has acted as a catalyst to advance hydrogen technologies. The Twenty-Year vision given in the document was aimed towards the long-term development of renewable based hydrogen technologies. In the interim, fossil fuels are to be a transitional resource. This is significant, because the technologies that use fossil fuels and that enable hydrogen in both the fuel infrastructure and vehicle technologies exist today, and can meet near term markets. Furthermore, as noted by industry participants in a hydrogen blueprint meeting in Sacramento, California, there are **no technical showstoppers** to implementing a near-term hydrogen fuel infrastructure for direct hydrogen fuel cell vehicles. Fundamentally, the technologies required are available but there are engineering development needs as well as codes and standards and other institutional issues to resolve.

A key driver for hydrogen vehicles is the California Zero Emissions Vehicle (ZEV) mandate. The ZEV mandate requires that by the year 2005, 10% of the total vehicles sold will be zero emission vehicles. Under the mandate, the number of “pure ZEVs” (i.e., hydrogen fuel cell vehicles or battery electric vehicles) will be 1% of the total vehicle market or about 10,000 hydrogen fuel cell vehicles.

## 1.3 DOE Hydrogen Program Strategic Approach

The DOE Hydrogen Research and Development Program's mission is to conduct research and engineering development in the areas of hydrogen production, storage, and utilization for the purpose of making hydrogen a cost-effective energy carrier for utility, buildings, and transportation applications. The program is being positioned to support the introduction of hydrogen technologies to meet California's ZEV mandate requirements, and the push for distributed generation.

The program is expanding the short-term applications of hydrogen through partnerships with industry that will allow improvements in efficiency, decrease emissions, and lower the cost of hydrogen production. Projects are being undertaken with fuel cell manufacturers to develop hydrogen based electricity storage and generation systems that will enhance the introduction and production of distributed systems. The program also aims to develop codes and standards and safe systems to facilitate the creation of a hydrogen infrastructure. Systems will be developed that are cost-effective and safe for use in hydrogen vehicles in urban non-attainment areas, in addition to the creation of on-board hydrogen storage systems. The program also aims to lower the cost of technologies that produce hydrogen directly from sunlight and water.

### 1.3.1 Production Goals

If fuel cell vehicles are going to be competitive on the open market, an infrastructure for the generation and distribution of hydrogen must be established. To compete with other energy carriers, such as

electricity, natural gas, and petroleum, the cost of generating hydrogen must come down. A system for distributing the fuel must also be commercially available.

- **Improving the efficiency and lowering the cost of fossil based and biomass-based hydrogen production processes to \$6-\$8/ MMBtu**

Initially, hydrogen utilized in fuel cells will be produced from natural gas. The competing option will be to burn the natural gas/hydrogen blends in combustion turbines or internal combustion engines. To make fuel cells competitive with respect to the combustion options, the cost differential between hydrogen and natural gas must be minimized. Toward this aim, the goal of \$6-\$8/ MMBtu production cost of fossil-based and biomass-based hydrogen was established. In addition, in order to support the transportation market, the Program has set a goal of \$12-\$15/ MMBtu (which is approximately 60-75 cents per gallon of gasoline before taxes, based on a fuel-cell vehicle with an equivalent of about 82mpg) for the cost of producing pressurized hydrogen at the refueling station.

Hydrogen can also be produced by the gasification of dedicated biomass crops for approximately \$6-\$8/ MMBtu. By adding CO<sub>2</sub> sequestration, both the natural gas and biomass strategies can be augmented. Hydrogen can be produced by these technologies and delivered to a vehicle less expensively than gasoline on a mile per gallon equivalent basis when compared with today's 28 miles per gallon efficiencies.

- **Advancing emission-free and renewable-based hydrogen production technologies towards commercial viability, with a target cost of \$10-\$15/ MMBtu**

In order to advance the mission relating to technologies that produce hydrogen from sunlight and water, the Hydrogen Program will pursue long-term electrolytic, photoelectrochemical, and photobiological research and development. The program has set a goal of producing electrolyzers at efficiencies greater than 92% for less than \$300/ kW.

### **1.3.2 Storage and Utilization Goals**

Hydrogen vehicles will not be cost effective unless storage is priced competitively. Market forces, particularly cost, will be the key driver bringing fuel cell vehicles to compliance with California's ZEV mandate. To facilitate the development of a hydrogen infrastructure to support fuel cell vehicles and ultimately electricity generation from hydrogen, the goals below were developed.

- **Demonstrating safe and cost-effective storage systems for use in stationary distributed electricity generation applications, and for on-board and stationary applications in urban non-attainment areas that will achieve 200-400 mile range**

A major improvement in hydrogen storage performance will be necessary for hydrogen to gain acceptance as an effective energy carrier. With intensive interest in mobile applications and as the amount of intermittent renewable electricity increases, hydrogen storage becomes an essential element of these systems. Current technology permits the physical storage, transport, and delivery of hydrogen, in gaseous or liquid form, in tanks and pipeline systems. These physical storage systems have been used in various stationary and mobile demonstrations, but the issues of safety and energy consumption require the development of advanced storage concepts based on advanced materials for physical storage and chemical storage mediums. The program aims to develop storage that will deliver greater than 5.5% hydrogen by weight at temperatures less than 110°C, for on-board vehicle storage.

- **Developing fuel cell and reversible fuel cell technologies as an efficient low-cost means of converting hydrogen into electric power**



In order to develop a hydrogen infrastructure, the end-use technologies must be developed and matured. Here, the primary technology is the fuel cell. In order for fuel cells to be the "work horse" hydrogen utilization tool, several technical hurdles must be overcome. Fuel cells must be run on hydrogen directly to prevent CO<sub>2</sub> emissions; fuel cell efficiencies must be increased and their cost must be lowered to make them competitive; and reversibly electrolyzer/fuel cell modules must be developed that can enable substantial reductions in overall system costs. The Program aims to produce PEM fuel cells for niche applications, such as small battery replacements that cost less than \$300/kW. In addition, the Program is striving toward reversible fuel cells having a round-trip efficiency of 70%, and a cost of less than \$600/kW and electrolyzers at a cost less than \$300/kW.

### 1.3.3 Technology Validation Goals

This focus area concentrates on validating nearer term technologies against a series of cost, performance, and safety objectives. This can include the integration of any combination of production, storage, transport, and utilization technologies, and is performed in collaboration with industry. These projects will help to facilitate hydrogen technologies' establishment as a viable application and ensure competitiveness with other technologies. Through the Technology Validation Program, DOE's Hydrogen Program will promote direct hydrogen fuel cell vehicles that meet the demands of California's ZEV mandate.

- **The goal of the Technology Validation is to support industry in the verification and demonstration of hydrogen systems in the utility and transportation sectors.**

Technology validation projects integrate components of novel and advanced technology into test-bed energy systems to evaluate their potential. Parallel development of advanced fossil-based and renewable-based production systems, as well as current and advanced storage and utilization technologies, will provide a set of critical experiences to industry as they evaluate the introduction of the technologies into niche markets.

The strategy of the technology validation is within the Technology Validation Plan. The Program will achieve its goals by operating under the following objectives:

1. Obtain industry participation through competitive solicitations for mid-term development and proof-of-concept testing
2. Integrate renewable energy resources with hydrogen storage in remote, distributed power scenarios
3. Test the viability of hydrogen production, storage, and refueling stations
4. Test the viability of hydrogen production, storage, and refueling stations within several clean clusters
5. Evaluate remote and residential "total" energy PEM fuel cell systems
6. Develop hydrogen-based operating experience acceptable to meet safety codes and standards.

### 1.3.4 Environmental Goals

The generation and consumption of energy is the largest single source of air pollution in the United States. Electricity produced from fossil fuels results in one-third of all carbon-based emissions. The oil-dependent transportation sector contributes another third. To cut emissions and reduce the effects of harmful urban pollutants, such as NO<sub>x</sub>, SO<sub>x</sub>, and CO, there must be a shift away from fossil fuel-based energy and an increasing dependence on renewable sources of energy. In response, the Hydrogen Program has set forth the goals of reducing emissions in urban non-attainment areas, and reducing global

greenhouse gas emissions. The goals are to displace 1.9 million tons of carbon by 2010 and 13.5 million tons of carbon by 2020. Emissions are to be reduced by 52,000 tons/year of NO<sub>x</sub>, 390,000 tons/year of CO, and 45.6 million tons/year of CO<sub>2</sub> by 2020.

### 1.3.5 Policy, Planning, and Analysis Goals

Analysis and technology transfer incorporates many of the activities formerly grouped under the titles of Systems Analysis and Integration, Technology Transfer, and Industry and Educational Outreach. This includes the identification and definition of research opportunities for hydrogen as an energy carrier through system and infrastructure evaluations and analyses. Analysis will be used to determine the economic feasibility of various scenarios through the calculation of life cycle costs of individual production, storage, transport, and end-use technologies, as well as overall systems. Projects such as technical brochures, fact sheets, and exhibits will all be evaluated and presented to the Program. As set forth in the Strategic Plan the goals of Policy, Planning, and Analysis include:

- **Ensuring that Federal R&D investments in hydrogen production, storage, distribution, and end-use technologies will provide the maximum value added to national strategic goals including global greenhouse emission mitigation**

The goal of supplying significant amounts of renewable hydrogen to the electricity supply and transportation markets in 20 to 30 years cannot be achieved with current budgets unless they are highly leveraged with other Federal programs and with industry. The key planning and analysis issue for the Program is how to define and maximize its "value-added" to the national and global transition to renewable energy.

- **Identifying and evaluating key market segments and market entry conditions for hydrogen utilization in transportation and in electricity generation at distributed and remote locations**

In order for policy makers to make rational decisions regarding the utilization of hydrogen, it is necessary that they receive the pertinent information and recommendations from the Program and industry. These recommendations must evolve from data developed from the development and validation components of the Program, and must incorporate reasonable and thorough systems analysis of hydrogen integrated pathways.

- **Developing and applying metrics to measure the Program's contribution to attaining national strategic energy goals and market share in key segments**

It is necessary for the program to develop a database that will incorporate cost, performance, reliability, lifetime, and other key characteristics for hydrogen technologies to contribute to national strategic energy objectives and compete in key market segments.

### 1.3.6 Outreach and Coordination Goals

In California, the public must also be aware of the air quality improvements that result from the use fuel cell vehicles and the ZEV mandate. The Program conducts various industry outreach, public outreach, and international activities including efforts in three major areas: workshops and conferences, exhibits and trade shows, and publications. These outreach and technology transfer activities span the entire program structure. The goal of the outreach is:

- **Conduct outreach and coordination to develop informed constituencies in the industrial and public sectors as part of a strategy to accelerate the commercialization of renewable hydrogen technologies.**

For hydrogen to act as an energy carrier, the public must be informed of the technology. The public must be made aware of the economic and environmental benefits of hydrogen technologies, the level of safety associated with hydrogen technologies, and industry's impressive safety record producing and using large quantities of hydrogen.

## 1.4 Responses to Recommendations

In addition to the aforementioned responses to recommendations from the NEP, the DOE Hydrogen Program also has responded to recommendations from the National Academy of Public Administrators (NAPA) and the National Research Council (NRC). In addition the Program holds an annual technical peer review of its projects.

### 1.4.1 National Academy of Public Administration

The Hydrogen Program has been responsive to the recommendations of NAPA. The following information outlines NAPA's recommendations and how the Hydrogen Program is responding.

- **Recommendation:** "Take a more proactive role in defining program goals, objectives, and content."
- ✓ **Response:** The Hydrogen Program Management Team revisited the Program goals and objectives to ensure conformity with EERE Strategic Plan targets.
  
- **Recommendation:** "Focus and consolidate the array of small individual projects, discontinuing the weakest efforts and activities that do not further EERE's mission and priorities, shifting resources to stronger programs, and exercising greater discretion in the choice of programs."
- ✓ **Response:** Recommendations from the Annual Peer Review Meeting were followed. See Section 1.4.3.
  
- **Recommendation:** "Clarify the roles and responsibilities of program and project manager, and make clear that their responsibilities are much broader than those of securing funds and authorizing funding actions, but continue through all phases of activities, including program and project execution and evaluation."
- ✓ **Response:** The roles and responsibilities of Headquarters Program Management involve defining policy and strategic goals and objectives. Project engineers in the field are responsible for budget reconciliation, and approval of invoices and reports for each competitively awarded project.
  
- **Recommendation:** "Review the status of long-standing cost sharing agreements to determine that the cost sharing ratios being applied are consistent with the current stages of development."
- ✓ **Response:** Project engineers in the field have reviewed all competitively awarded projects for their cost sharing obligations.
  
- **Recommendation:** "Minimize special and unique reporting requirements, and structure reports to facilitate reconciliation with the official DOE reports, while recognizing the continued need of program and project managers for specific direct reporting."

- ✓ **Response:** The Hydrogen Program has fully implemented the Strategic Management System (SMS) key milestones and key milestone reports.
- **Recommendation.** “Structure a regular EERE-level review to report program progress for all significant activities and accrued costs. Review accrued costs in relation to technical progress to ensure that appropriate data is available.”
- ✓ **Response.** The Hydrogen Program regularly updates its key milestones list in the SMS that can be reviewed by DOE management.

### 1.4.2 National Research Council

The Hydrogen Program has also been responsive to the recommendations of the NRC. The findings and recommendations of NRC are listed below, as well as the Hydrogen Program’s response. The NRC findings and recommendations are quoted from “Renewable Power Pathways: A Review of the U.S. Department of Energy’s Renewable Energy Programs”.

- ≡ **Finding:** “The DOE has a number of programs involving the use of hydrogen, which has created a confusion of effort and responsibility.”
- **Recommendation:** “The Hydrogen Research Program should be reoriented with a longer term perspective and broader participation by other elements of the U.S. Department of Energy’s (DOE’s) energy research establishment. The Office of Power Technologies (OPT) should concentrate on research aimed at the production of hydrogen from renewable resources and secondarily on hydrogen storage for distributed power generation. DOE should consider establishing a central point for the coordination of all research on “hydrogen systems,” including OPT’s hydrogen research and related activities in the DOE’s Offices of Transportation Technologies, Fossil Energy, and Science.”
- ✓ **Response.** DOE has already established a central point for coordination of hydrogen activities. Acting on the requirements of the Matsunaga Act of 1990 and renewed in the Hydrogen Future Act of 1996, the Secretary established this central point as the OPT Hydrogen Program. This has proven very beneficial for DOE in that it allows the Department to maintain a balanced, managed program that meets the specific program objectives that enhances hydrogen’s ability to enter the market place. Hydrogen can be made from many diverse feedstocks including fossil fuels, biomass, and water. The Hydrogen Technical Advisory Panel (HTAP) and hydrogen stakeholders have endorsed a balanced approach that includes hydrogen production from all of these resources. The Hydrogen Program coordinates this effort, which is carried out by the various DOE Offices without duplication of effort.

The Hydrogen Program works with the Offices of Transportation Technology and Fossil Energy through the issuing of joint solicitations and co-funded projects. Hydrogen Program Managers also interface with counterparts at the Office of Science to ensure that the latter’s basic research supports the OPT applied programs.

Section 2.4 in Chapter 2 provides details regarding the Hydrogen Program’s crosscutting efforts.

- ≡ **Finding:** “The Hydrogen Research Program does not seem to have a clear methodology for selecting projects.”

- **Recommendation:** “The Office of Power Technologies should establish a systematic method of setting priorities focused on how resources can best be used. Regular performance-based reviews of projects would improve the efficiency of the program substantially.”
- ✓ **Response.** The Hydrogen Program provided NRC with a strategic plan in which it established specific performance metrics for the critical production, storage, and utilization activities, as set forth in the Matsunaga Act. Through HTAP and stakeholder meetings, the Hydrogen Program established a strategic plan with goals, objectives, and a timeline. The goals and objectives are continuously reviewed and priorities are set. These priorities are implemented through competitive solicitations, which are reviewed annually by panels of experts who provide recommendations.
- ▢ **Finding:** “The committee agrees with HTAP’s concern that too much emphasis is placed on relatively near-term ‘technical validation’ and the establishment of a distribution infrastructure at the expense of badly needed long-term exploratory and innovative R&D.”
- **Recommendation:** “The Office of Power Technologies should defer its plans for infrastructure development involving hydrogen fueling stations and fuel cells until a practical process for producing hydrogen from renewable resources is in view and a demand for hydrogen begins to emerge.”
- ✓ **Response.** The Hydrogen Program recognizes a commitment to maintaining long-term R&D and dedicates a significant portion of its budget to this. However, Section 104 of the 1996 Hydrogen Future Act requires the DOE to assign high priority to commercialization. The need for entry to the market place demands a near-term effort. The priorities and program emphasis that the Hydrogen Program follows, has been reviewed by HTAP and the hydrogen stakeholders. Therefore, the Hydrogen Program does not agree with this NRC finding due to its need to comply with the legislative mandate.
- ▢ **Finding:** “Some of the sources and methods for the production of hydrogen that OPT is investigating (i.e., hydrogen for fuel cells or transportation uses) seem better suited to other DOE R&D programs.”
- **Recommendation:** “The Hydrogen Research Program should focus on the production of hydrogen from all renewable energy resources, including biological methods of production. If the source of hydrogen is natural gas, the program must make a convincing case that the program can produce a superior product for the market. Alternate technologies (including fuel cells) that use natural gas directly should only be used as a reference for setting the goals of the program and should not be the major focus of the program.”
- ✓ **Response.** The Hydrogen Program funds projects that meet the goals of its Strategic Plan. The Program has established a dual-path strategy in which both off-board and on-board reforming is addressed. The Program shares responsibility for off-board reforming and subsequent on-board hydrogen storage with the Office of Transportation Technologies (OTT). Early introduction of the off-board reforming option by the Hydrogen Program has led to enabling the on-board hydrogen option. The joint-effort is manifested by joint solicitations and co-funding. There is no duplication of effort. OTT has the sole responsibility for the on-board reforming options. The strategy has been explained to HTAP and to hydrogen stakeholders and has been approved.

The Strategic Plan supports a transition through fossil fuels to enable the eventual implementation of renewable hydrogen. The Hydrogen Program’s fossil-based hydrogen research is for these transition purposes and does not duplicate research in other DOE programs. For example, OTTs’ program includes developing reformers, but these are for transportation fuels. While the Hydrogen Program is also looking at reformers, its research is aimed at small reformers that can be mass-produced and that

can convert natural gas to hydrogen at distributed generation facilities including hydrogen refueling stations.

### **1.4.3 The Annual Peer Review**

As part of our comprehensive management approach, the projects funded by the Hydrogen Program are independently reviewed by panels of experts. In fiscal year 2001, at a 3-day meeting in April, 18 reviewers evaluated seventy-four projects. These projects were presented and reviewed in two parallel sessions, Production and Technology Validation; and Storage, Utilization, Safety and Analysis, and Technology Transfer. Criteria included appropriate efforts being made and results of specific goals and objectives, timing and ability to meet milestones, future plans and collaborative efforts.

#### **1.4.3.1 General Comments**

Given the difficulty of making significant penetration of the transportation sector, the program's focus in this area needs to be reexamined and reinforced through analysis. The utility sector provides a greater opportunity for near term market penetration owing to market pull and availability of mature technology.

Highest priorities should be placed on storage, with emphasis on on-board storage technology that shall satisfy the program goals. Ongoing projects should be reassessed as to prospects for success and either discontinued or assigned a level of funding consistent with more fundamental research.

#### **1.4.3.2 Technology Areas**

Although compressed gas offers near term options for on-board storage, novel hydrides appear to offer a better option. However, safety concerns about the use of these materials must be addressed prior to making major funding commitments.

Stationary storage systems might be considered a priority for future projects as should reversible fuel cells for electrolysis and power generation.

Commitments to hydrogen production need to be reassessed in terms of achieving success. Higher risk technologies should be assigned funding levels more consistent with their ability to achieve success.

It was recommended that technical and/or economic analyses be made on all projects. These efforts should be expanded to provide the necessary focus and guidance to the program. Independent analysis must be made on the Technology Validation projects to ensure they are not ahead of the research and development phase and they can achieve the program's economic goals. All of these analyses should be performed by independent investigators or groups and the assumptions used by these investigators must be verified.

#### **1.4.3.3 Project Recommendations**

The reviewers recommended eleven projects should be assessed for termination. Four of these projects were focused on long-term production technologies, two on long term storage concepts, four on near term production projects, and one analysis project.

Five projects will be terminated based on the reviewer recommendations and our concurrence with their assessment. One project, Big Sky Fuel Cell Program, was a Congressional earmark that will be completed this year. The remaining projects are being assessed using a systems analysis method developed for the program. One key component of this analysis is whether the technologies can achieve the Program's economic goals. Once the analysis is complete, the management team will decide whether

it is necessary to terminate the projects, change the priority of the research, or require additional experimental results to be used for additional analysis.

## **2.0 TECHNICAL ORGANIZATION**

### **2.1 Approach**

The techniques employed by the emphasize state-of-the-art methods for: (1) genetic engineering to develop biological systems that can produce hydrogen directly from water or carbon-rich substrates such as the syngas produced from gasification of biomass; (2) engineering and manufacturing of high performance semiconductors that will directly convert photons (light energy) to hydrogen by splitting water; (3) developing newer high-efficiency methods to thermally break down fossil feed stocks and biomass to produce high purity hydrogen; and (4) producing engineered materials for high performance storage systems such as carbon nanotubes and fullerenes that can adsorb large volumes of hydrogen.

### **2.2 Objectives**

The objectives of the Hydrogen Program are to develop the critical technologies for hydrogen systems and support a vision of a sustainable energy future that includes hydrogen and electricity as the energy carriers. The accomplishment of these objectives will lead to improved energy use and efficiency, lower environmental emissions, and fuel use flexibility.

The Program supports the following activities: (1) developing and integrating the technology base for producing hydrogen using fossil and renewable sources; (2) developing advanced material and delivery systems for storage and transport options; (3) evaluating safety and reliability issues associated with utilization technologies; (4) performing technical and economic analyses on component technologies and processes; and (5) demonstrating hydrogen technologies within integrated energy systems, with strong industry collaboration.

### **2.3 Management Structure**

The Hydrogen Program is managed by the Department of Energy, with technical oversight and management assistance provided by its technical management group; National Renewable Energy Laboratory (NREL), Sandia National Laboratories (SNL) and Los Alamos National Laboratories (LANL). DOE provides technical and programmatic guidance, sets budgetary marks and establishes programmatic goals. The Program organization is shown in Figure 2.1. Headquarters activities are led by the Hydrogen Program Management Team.

The DOE Golden Field Office is responsible for coordination of the Program's cost-shared collaborative agreements. This includes project and financial management, and the issuing, coordinating, and evaluating of the Hydrogen Program's solicitations.

A group of technical managers, made up of scientists and engineers within the program also provide technical guidance and coordinate within the areas of thermal production, photoelectrolytic and photobiological production, storage, and utilization R&D.

The management team is involved with the planning efforts through technical reviews of proposals, annual peer review, and strategic planning meetings. Additionally, the NREL Program Office plans and executes the HTAP meetings, and produces and distributes all publications associated with the Panel and its subcommittees and reviews all production projects. SNL manages those validation projects for remote power applications, and reviews all storage projects and hydride development and LANL is conducting research on fuel cells.



HTAP, as mandated by the Matsunaga Act and amended by the Hydrogen Future Act, advises DOE management in carrying out the Program. The Panel members, nominated by the Secretary of Energy, represent industry, universities, financial and environmental organizations, and address issues such as developing market-sensitive transition paths from near-term to longer-term programmatic objectives.

The National Hydrogen Association (NHA), which is comprised of industry members, leads the DOE's activities in the development and promulgation of codes and standards related to the safe use of hydrogen. Widespread hydrogen use will require that safety be intrinsic to all processes and systems to ensure the public's complete confidence in hydrogen as a fuel. NHA has taken a lead role in writing new standards through the International Standards Organization, Technical Committee 197, to push forward standards for the safe handling of hydrogen. In addition, DOE has funded a consultant to support the NHA to promulgate new building codes in the United States. This consultant is an expert in working with the International Code Council (ICC). At his request, the ICC created an Ad Hoc Committee (AHC) on hydrogen technologies. This group is supported by the Hydrogen Program through funded experts conducting applied research and development in areas of interest. The AHC is reviewing all of the existing building codes for portable and vehicular fuel cells using hydrogen as a fuel and will recommend to the full ICC any modifications or additions that are required to introduce these technologies into the marketplace.

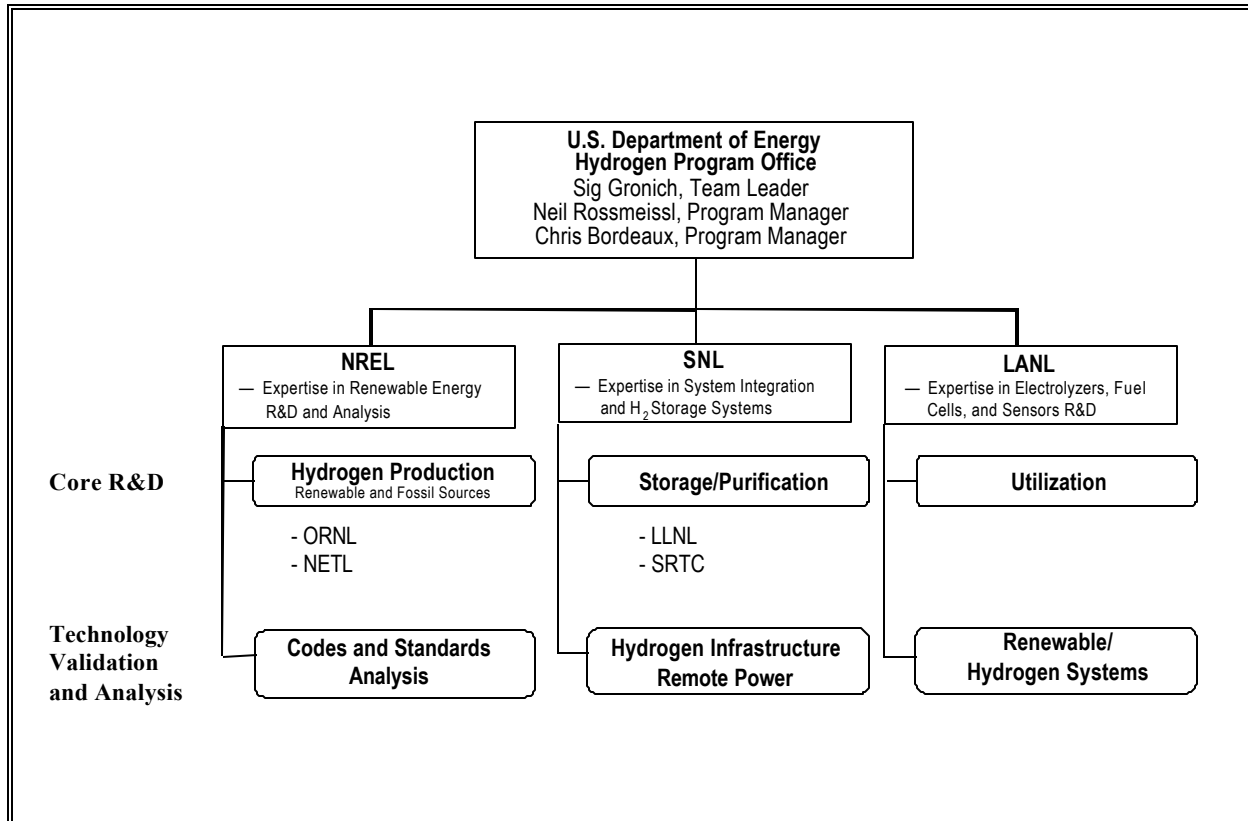
## **2.4 Hydrogen Program Organization**

The Hydrogen Program incorporates technical and management assistance provided by key program participants to guide the Program's management and direction, which is established by a DOE Headquarters Management Team. The Hydrogen Technical Advisory Panel (HTAP), NHA, NREL, SNL, LANL, and other Program participants submit input to the Program through both formal and informal mechanisms. These groups provide DOE with recommendations on the implementation and conduct of the Program, multi-year planning and resource allocation between technical and analytical issues. Additionally, independent technical review teams provide DOE with insights on the progress and direction of research and development, and a means by which researchers and industry can exchange information. Technology Road Maps, outlining the path over the next five years toward meeting these objectives, has been used as program guidance. DOE now intends to produce Technology Road Maps that outline the path over the next ten years.

The development of broad-based hydrogen energy systems necessitates interaction and cooperation among a number of crosscutting research and development projects and technologies within the Department and other Federal agencies. The Hydrogen Program is charged with the responsibility (via the Matsunaga and Hydrogen Future Act) to provide this Federal coordination role. DOE has entered into several collaborations in R&D and technology validation with the DOE Offices of Transportation Technologies, Building Technologies, Fossil Energy, and Science as well as the Defense Advanced Research Programs Agency, Defense Conversions Program, Department of Transportation (DOT) and the National Aeronautics and Space Administration (NASA). Crosscutting efforts include combined solicitations, interactive meetings, coordinated peer reviews, and collaborative projects.

The program goals and objectives are met by funding projects within universities, National Laboratories, and industry; monitoring the performance of projects; conducting an Annual Peer Review of all projects; reviewing all technical and programmatic plans with HTAP; circulating monthly program status reports to all of the program principal investigators (PIs) to facilitate communication; and disseminating hydrogen information through publications, participation in technical meetings, and substantive contacts with stakeholders. The activities funded by the Program are classified into three focused areas: a) Core R&D, b) Technology Validation, and c) Analysis and Technology Transfer. As a result of increased Program funding, many activities that have proven successful R&D phases, are now moving into the technology validation area.

**Figure 2.1**  
**DOE Hydrogen Program Organization**



### **3.0 PROGRAM ELEMENTS**

Each of the projects described below is accompanied by a milestone (Gantt) chart. Critical milestones are represented by stars in the charts.

#### **3.1 R&D on Hydrogen Production, Storage and Utilization**

The objective for this area is to develop critical cost-effective technologies by conducting research and development in the areas of production, storage, transport, and utilization. The work is conducted at universities, national labs, and industry as shown in the table accompanying each section.

##### **3.1.1 Hydrogen Production Research Projects**

The FY 2002 hydrogen production projects, summarized in Table 3.1 and 3.2, are broken up into four categories. These include fossil-based and biomass-based production, and electrolytic and photobiological processes. Separation techniques are included in “fossil-based production”, and photoelectrochemical processes are included in the “electrolytic category”.

<b>Table 3.1</b> <b>Fossil/Biomass Based Production</b>		
<b>Goal: Improve the efficiency and lower the cost of fossil-based and biomass-based hydrogen production processes to \$6-\$8/MMBtu</b>		
<b>Category</b>	<b>Project</b>	<b>Researchers</b>
<i>Fossil-Based Production</i>	Thermal Dissociation of Methane Using a Solar-Coupled Aerosol Flow Reactor	National Renewable Energy Laboratory
	Production of H <sub>2</sub> by Superadiabatic Decomposition of Hydrogen Sulfide	Gas Technology Institute
	Thermocatalytic CO <sub>2</sub> – Free Production of Hydrogen from Hydrocarbon Fuels	Florida Solar Energy Center
	Novel Catalytic Fuel Reforming	InnovaTek, Inc.
	Engineering Development of Ceramic Membrane Reactor Systems for converting Natural Gas to Hydrogen and Synthesis Gas for Liquid Transportation Fuels	Air Products and Chemicals, Inc.
	Integrated Ceramic Membrane System for H <sub>2</sub> Production	Praxair, Inc.
	Production of Hydrobromic Acid from Bromine and Methane for Hydrogen Production	SRT Group
<i>Biomass-Based Production</i>	Fluidizable Catalysts for Hydrogen Production from Biomass Pyrolysis/Steam Reforming	National Renewable Energy Laboratory
	Biomass Pyrolysis for Hydrogen Production	Jet Propulsion Laboratory
	Supercritical Water Partial Oxidation	General Atomics
	Biohydrogen Production from Renewable Organic Wastes	Iowa State University
	Bio-production of Hydrogen Using Thermophilic Bacteria	National Energy Technology Laboratory
	Hydrogen Production from Post-Consumer Wastes	National Renewable Energy Laboratory
	Biological H <sub>2</sub> from Fuel Gases and from Water	National Renewable Energy Laboratory
	Bioreactor Development for Biological H <sub>2</sub> Production	National Renewable Energy Laboratory
	Biomass Derived Hydrogen from a Thermally Ballasted Gasifier	Iowa State University
<i>Separation &amp; Purification</i>	Separation Membrane Development	Westinghouse Savannah River Technology Center
	Defect-free Thin Film Membrane for H <sub>2</sub> Separation & Isolation	Sandia National Laboratories

## FOSSIL-BASED PRODUCTION

### Thermal Dissociation of Methane Using a Solar-Coupled Aerosol Flow Reactor- National Renewable Energy Laboratory

The overall goal for this project is to demonstrate, at pilot scale, a solar thermal process for splitting methane to hydrogen and carbon black with reactor efficiencies greater than the 50% required to achieve acceptable economics for a full-scale system.

The basis of this concept is the high temperature thermal dissociation of methane in a solar heated aerosol flow reactor. Methane is dissociated to carbon black and hydrogen in the following reaction:



Highly concentrated sunlight can be used to generate the high temperatures needed and provides an environmentally clean option for the production of hydrogen. The solid carbon black can be sold for increased economic value (over the sale of hydrogen) or can be more easily stored or sequestered than can carbon dioxide. Technical feasibility of driving this reaction to high conversion (over 90%) with concentrated sunlight has been shown in small-scale experiments at NREL. Preliminary economic analysis shows that the process is attractive when both products are sold and particularly if high value carbon black can be produced (5M kg/yr H<sub>2</sub> solar thermal plant: \$0.35/lb carbon black price yields \$6/MMBtu hydrogen). The process is environmentally benign as indicated by preliminary life cycle analysis conducted at CU.

Additionally, a number of industrial partners have been brought into the project by CU. These include BP Hydrogen and EPRI, where both are providing in-kind cost share to CU's GFO cost-share requirements. Discussions with Chevron-Phillips (high quality carbon black producer) are ongoing.

#### **Task 1: Experimental evaluation of an improved reactor system at the High-Flux Solar Furnace**

Conduct on-sun experiments using reactor system designed and fabricated in FY01 by the University of Colorado. Evaluate improved analytical systems, particularly the measurement of reactor temperature. Maintain appropriate safety procedures and documentation to insure safe operation of experiments using flammable gases

#### **Task 2: Plant design/Economic analysis**

Develop pilot scale plant optical concepts. Analyze optical performance of selected concepts. Update economic analysis with improved reactor algorithms based on experimental kinetics results. Design pilot scale reactor/secondary concentrator concepts. Develop pilot scale designs for unit operations and balance of plant components.

<b>Thermal Dissociation of Methane Using a Solar-Coupled Aerosol Flow Reactor</b> <b>National Renewable Energy Laboratory</b>						
Task Designation/Milestone		FY2002				2003
	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4	Qtr 1
<b>Task 1: Experimental evaluation of an improved reactor system at the High-Flux Solar Furnace</b>						
Complete reactor shakedown experiments		◆				
<b>Task 2: Plant design/Economic analysis</b>						
Revised economic analysis of pilot plant				★		
FY2002 Begins October 1, 2001      ★ = Critical Milestone      ◆ = Milestone						

## **Production of H<sub>2</sub> by Superadiabatic Decomposition of Hydrogen Sulfide – Gas Technology Institute**

The goal of this project is to develop a novel process for the production of low cost hydrogen and sulfur by enhanced thermal decomposition of hydrogen sulfide, with no carbon dioxide emissions.

The proposed process uses superadiabatic combustion, (SAC), to thermally decompose H<sub>2</sub>S to hydrogen and sulfur. A portion of the H<sub>2</sub>S is combusted to provide the energy required for decomposition. SAC is based on combustion in the presence of a porous medium with intense heat exchange. As a result, the flame temperature in SAC can significantly exceed the adiabatic flame temperature for the mixture.

The objective of Phase 1 of the project was to develop a detailed process development roadmap for the SAC-based H<sub>2</sub>S decomposition process, leading to technical and economic validation of the process in Phase 2, outlining the steps required and costs involved in moving the SAC technology to a condition of readiness for field testing in a commercial facility. The work completed in Phase 1 included modeling of the superadiabatic combustion of H<sub>2</sub>S for development of an integrated thermochemical model, a process design study for evaluation of SAC process design options, including reactor configuration, operating conditions, and product/byproduct separation schemes. A lab-scale experimental system was designed and a detailed test plan was developed for process design optimization and model verification testing in Phase 2.

The objective for Phase 2 of the project is to develop the necessary experimental data to demonstrate the technical and economical viability of the process and to update the technology for industrial partners' market evaluation and demonstration plans.

### **Task 1: Construction of Lab-Scale Unit**

A lab-scale SAC-Based H<sub>2</sub>S decomposition reactor system will be designed and constructed to obtain the necessary experimental data to verify the technical feasibility of the process. The reactor consists of a fixed-bed packed with alumina pellets where hydrogen sulfide is thermally decomposed to hydrogen and sulfur. In this unit H<sub>2</sub>S-rich waste gas is mixed with air and fed to the SAC reactor. Off-gas leaving the SAC reactor is cooled to condense sulfur vapors and liquid sulfur is drained and collected. Cooled off-gas is analyzed and treated before discharged to the atmosphere.

### **Task 2: Technical Feasibility Verification**

In this task, based on the test plan developed in Phase 1, a number of tests will be conducted in the lab-scale SAC reactor unit to determine the effects of operating parameters on the performance of the process. The parameters to be studied in these tests will include inlet fuel gas composition, equivalence ratio, gas residence time, temperature, and the porous media material.

### **Task 3: Thermodynamic and Kinetic Modeling**

The data generated in Task 2 will be thoroughly analyzed to verify the technical feasibility of the process. Based on these results, the computer model used in Phase 1 for predicting SAC performance will be updated. The process design for SAC will be updated and optimized to maximize system efficiency and hydrogen production. The system cost will be updated based on the optimized process design.

### Task 4: Process Economics and Market Analysis

The results obtained in Task 3 will be used to validate the market and economic viability of the process. Evaluation of potential markets will include analysis of both the sulfur recovery markets as well as hydrogen and sulfur end-user markets. Factors considered in the analysis will include:

- Current and projected hydrogen and sulfur prices
  - Status of competing hydrogen production and combined hydrogen and sulfur recovery processes under development
  - Current size and demand projections for the various hydrogen market sectors, including petroleum refining, ammonia, methanol, and fuels
  - Current size and demand projections for sulfur market sectors, including sulfuric acid, fertilizers, etc.
- Information on the sulfur recovery, hydrogen and sulfur markets will be used to determine the most favorable potential settings for deployment of the SAC hydrogen production technology.

### Task 5: Data Analysis and Program Management

The data generated in the above tasks will be analyzed and a final will report will be prepared detailing all results and recommendations from the project. All work will be coordinated with DOE project manager and our project team.

Production of H <sub>2</sub> by Superadiabatic Decomposition of Hydrogen Sulfide Gas Technology Institute (GTI)						
Task Designation/Milestone	FY2002					2003
	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4	Qtr 1
<b>Task 1: Construction of Lab-Scale Unit</b>						
Complete construction of the unit		◆				
Complete Unit Shakedown		◆				
<b>Task 2: Technical Feasibility Verification</b>						
Complete Parametric Studies				★		
<b>Task 3: Thermodynamic and Kinetic Modeling</b>						
Update kinetic model				◆		
<b>Task 4: Process Economics and Market Analysis</b>						
Completion of market and economic analysis				◆		
<b>Task 5: Data Analysis and Program Management</b>						
Completion of data analysis and final report					◆	

FY2002 Begins October 1, 2001      ★ = Critical Milestone      ◆ = Milestone



## **Thermocatalytic CO<sub>2</sub>-free Production of Hydrogen from Hydrocarbon Fuels – Florida Solar Energy Center**

The main objective of this project is the development of an economically viable thermocatalytic process for production of hydrogen and carbon from gaseous or liquid hydrocarbon fuels with minimal environmental impact. The chief technical goal is to accomplish CO<sub>2</sub>-free production of hydrogen and carbon via efficient single-step thermocatalytic decomposition (TCD) of hydrocarbon fuels over carbon-based catalysts in air/water-free environment. This approach would result in drastic reductions in CO<sub>2</sub> emissions (compared to conventional hydrogen production processes), thus obviating the need for potentially costly and ecologically uncertain CO<sub>2</sub> sequestration. Due to its simplicity and the lack of bulky and expensive gas conditioning and purification stages (water gas shift, preferential oxidation, etc.), TCD approach could be particularly advantageous for the decentralized (on-site) hydrogen production. The combination of TCD reactor with PEM fuel cell could be potentially applicable to distributed power generation, including residential, industrial, and transportation systems.

FY2002 activities include the following tasks and sub-tasks:

### **Task 1: Improve Catalyst Stability and Process Sustainability**

#### **Sub-task 1-1: Improve catalyst stability and process sustainability**

In this sub-task the catalyst long term stability and the process sustainability will be improved via internal (in-situ) and external reactivation of carbon catalysts. Researchers at the Florida Solar Energy Center (FSEC) will determine the extent of carbon catalyst activation as a function of operational conditions (e.g., temperature, residence time, etc.).

#### **Sub-task 1-2: Optimize hydrogen production yield**

In this sub-task FSEC will explore the methods to enhance catalytic activity of carbon catalysts, e.g., via surface structure modification. The selectivity toward hydrogen production yield will also be optimized. The techniques to remove potentially harmful unsaturated and aromatic hydrocarbons from the hydrogen gas will be determined (e.g. via catalytic hydrogenation).

#### **Sub-task 1-3: Determine the effect of moisture, sulfur and other impurities on the process efficiency**

The purpose of this sub-task is to determine to what extent moisture, sulfur and other impurities present in industrial grade hydrocarbon fuels could affect the carbon catalyst activity and long term stability.

### **Task 2: Develop and Demonstrate a Scaled-up Thermocatalytic Reactor (TCR) for CO/CO<sub>2</sub>-free Production of Hydrogen**

#### **Sub-task 2-1: Design a scaled-up TCR**

In this sub-task FSEC will identify the critical issues required to design and fabricate an efficient TCR for CO/CO<sub>2</sub>-free production of hydrogen. They will evaluate different conceptual designs for the scaled-up reactor. A TCR with the targeted power range of 3-5 kW will be designed.

#### **Sub-task 2-2: Fabricate and demonstrate TCR (3-5 kW)**

(Critical Milestone). In this sub-task FSEC will fabricate TCR in the power range of 3-5 kW. TCR will be packaged into a compact configuration. The power density of TCR will be optimized, targeting 1 kW<sub>th</sub>/L. The performance characteristics of TCR with regard to throughput and hydrogen yield using different fuels will be determined. Safety issues related to operation of TCR and handling carbon product will be addressed.

**Sub-task 2-3: Operate TCR on commercial hydrocarbon fuels**

In this sub-task FSEC will conduct a comprehensive performance testing of TCR using commercial hydrocarbon fuels, e.g., natural gas, propane and gasoline. The effect of fuel contaminants on the purity of hydrogen and carbon products will be determined. FSEC will explore the techniques to purify hydrogen gas from probable impurities (e.g. H<sub>2</sub>S, CO/CO<sub>2</sub>, etc.) down to ppmv levels.

**Task 3: Evaluate the Effect of Carbon Product on Process Economics****Sub-task 3-1: Evaluate the markets for carbon products**

In this sub-task FSEC will evaluate a market value of carbon products produced in the process. A thorough market study will be conducted to find a demand for carbon products, without saturating the market. The outlook for the energy use of carbons (e.g., as a quality fuel supplement for powdered coal) will be evaluated.

**Sub-task 3-2: Identify potential application areas for carbon products**

The potential markets for carbon products will be evaluated (in cooperation with industry). FSEC will produce sample quantities of carbon products and send them to our industrial collaborators. Particular attention will be given to such potential application areas as an energy storage, composite materials and environmental clean-up.

**Sub-task 3-3: Conduct techno-economic and system analysis of the thermocatalytic process**

In this sub-task FSEC will conduct techno-economic and system analysis of the thermocatalytic process for large and small (on-site) hydrogen production units. Sensitivity analysis, particularly, with regard to the effect of carbon sale on the process economics, will be conducted. The effect of fuel desulfurization on the hydrogen cost will be estimated. The ecological and economical advantages of TCD process over methane steam reforming coupled with CO<sub>2</sub> sequestration will be evaluated.

<b>Thermocatalytic CO<sub>2</sub>-free Production of Hydrogen from Hydrocarbon Fuels</b> <b>Florida Solar Energy Center</b>						
Task Designation/Milestone	2002					2003
	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4	Qtr 1
<b>Task 1: Improve Catalyst Stability and Process Sustainability</b>						
Demonstrate improvement in catalyst stability and sustainability				◆		
Complete studies on the effect of moisture and sulfur				◆		
<b>Task 2: Demonstrate Scaled-up Thermocatalytic Reactor (TCR) for CO/CO<sub>2</sub>-free Production of Hydrogen</b>						
Complete design of a scaled-up TCR					◆	
Fabricate and demonstrate TCR (3-5 kW range)					★	
Operate TCR on commercial hydrocarbon fuels						◆
<b>Task 3. Evaluate Effect of Carbon on Process Economics</b>						
Complete market study for carbon products						◆
Complete techno-economic and system analysis						◆

FY2002 Begins October 1, 2001      ★ = Critical Milestone      ◆ = Milestone

## **Novel Catalytic Fuel Reforming – InnovaTek, Inc.**

The ultimate goal of this 4-year cooperative project is to develop a microchannel catalytic reactor for the production of clean hydrogen by the catalytic reforming of natural gas. Advanced membrane separation technology will be compared to catalyzed CO conversion processes to select an approach that will provide a CO-free output stream of hydrogen to be used as a fuel stream for a compatibly sized PEM fuel cell for electrical generation.

By applying the advantages of microtechnology and advanced fuel-flexible catalysts, InnovaTek's fuel reformer will utilize currently available fuels such as natural gas and be adaptable to methanol and other renewable biomass energy sources when they are more widely distributed. This approach to fuel processing provides a revolutionary breakthrough in terms of system size, weight, and dynamic response when compared to more conventional processing carried out in standard packed bed reactors.

The objectives for FY 2002 are to integrate components and demonstrate an alpha-stage prototype by:

- Determining optimized catalyst and membrane compositions and operating conditions
- Defining specific requirements and testing candidates for process controls and peripheral components for natural gas feed stream supply; and
- Integrating components and achieve cost competitive reactor design through manufacturing engineering of a commercially viable system.

In FY 2003 Innovatek will demonstrate operating capability with the reformer unit attached to a compatibly sized fuel cell.

### **Task 1: Catalytic steam reforming in microchannel configuration**

Subtask 1.4: Effect of catalyst composition on activity, selectivity, and fabrication costs

Subtask 1.5: Determination of optimal reforming conditions

- Milestone: Complete 1000-hr continuous reforming run

### **Task 2: Hydrogen purification using advanced membrane separation technology**

Subtask 2.5: Optimize membrane composition, thickness, geometry, and operating procedures

Subtask 2.6: Compare membrane performance to WGS approach for CO clean-up

- Milestone: Final decision on hydrogen purification strategy

### **Task 3: Thermal management using microchannel heat exchangers and internal burner**

Subtask 3.4: Fabricate and test burner for chemistry of membrane reject stream

Subtask 3.5: Fabricate and test thermal management system for catalyst reactor and membrane components

- Milestone: Establish optimum system for thermal management

### **Task 4: Process and component integration**

Subtask 4.1: Integrate heat exchangers and internal burner with catalytic reformer and membrane components and assemble integrated reactor. Design and assembly experience from reactor and burner testing will provide the basis for improved design for manufacturing to reduce system costs.

- Milestone: Complete fabrication of integrated prototype system

Subtask 4.2: Test integrated system

- **Key Milestone :** Complete test runs of fully integrated system

Subtask 4.3: Update the thermal-process model to include performance analysis gained from operation of the integrated prototype system.

Novel Catalytic Fuel Reforming InnovaTek						
Task Designation/Milestone	2002					2003
	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr4	Qtr 1
<b>Task 1: Catalytic steam reforming in microchannel configuration</b>						
Optimize catalyst composition	◆					
Evaluate reforming conditions			◆			
Complete 1000-hr continuous reforming run			◆			
<b>Task 2: Hydrogen purification using advanced membrane separation technology</b>						
Optimize membrane composition & operating procedures				◆		
Examine WGS approach for CO clean-up			◆			
Final selection of hydrogen purification strategy				◆		
<b>Task 3: Thermal management using microchannel heat exchangers and internal burner</b>						
Fabricate and test burner		◆				
Fabricate and test thermal management system			◆			
Finalize thermal management system			◆			
<b>Task 4: Process and component integration</b>						
Integrate heat exchangers and internal burner with reformer and CO clean-up components					◆	
Complete fabrication of integrated prototype system					◆	
Test integrated system						◆
Complete test runs of fully integrated system						★
Update thermal process model						◆

FY2002 Begins October 1, 2001      ★ = Critical Milestone      ◆ = Milestone

## **Engineering Development of Ceramic Membrane Reactor Systems for Converting Natural Gas to Hydrogen and Synthesis Gas for Liquid Transportation Fuels – Air Products and Chemicals, Inc.**

The objective of this program is to research, develop and demonstrate a novel ceramic membrane reactor system for the low-cost conversion of natural gas to synthesis gas and hydrogen for liquid transportation fuels: the ITM Syngas and ITM H<sub>2</sub> processes. Through an eight-year, three-phase program, the technology will be developed and scaled up to obtain the technical, engineering, operating and economic data necessary for the final step to full commercialization of the hydrogen generation and syngas for GTL processes.

Phase 2 of the program, Engineering and Development of an ITM Syngas / ITM H<sub>2</sub> PDU and SEP, was initiated in FY2000. Phase 2 extends for 3.5 years and will validate process concepts in two stages of scale-up, and create an engineering, operating and economic database.

### **Task 2.1: Commercial Plant Economic Evaluation**

Air Products, Chevron, McDermott and Norsk Hydro will develop advanced ITM Syngas and ITM H<sub>2</sub> processes, with input from the University of Alaska. The economics of operation at the commercial plant scale will be evaluated based on the results of the Phase 2 program, including Process Development Unit (PDU) operation.

### **Task 2.2: Materials and Seals Development and Evaluation**

Air Products, Eltron Research and Penn State University will obtain laboratory scale statistical performance and lifetime data under ITM Syngas and ITM H<sub>2</sub> process conditions. Ceramtec will fabricate the ITM membrane / seal samples for testing, with input from Norsk Hydro, Pacific Northwest National Laboratory and the University of Pennsylvania. Based on test results, membrane materials, catalysts, and seals will be selected for scale up in the Subscale Engineering Prototype (SEP).

### **Task 2.3: ITM Syngas Membrane and Module Design and Fabrication**

Air Products, Ceramtec and McDermott will design membrane reactors for the ITM Syngas/ ITM H<sub>2</sub> processes at the PDU, SEP and commercial scales. Ceramtec will fabricate sub-scale membrane modules for testing in the PDU. Ceramtec will scale up the fabrication of the membrane reactor modules in a Production Development Facility (PDF) to supply the requirements of the SEP.

### **Task 2.4: Nominal 24 MSCFD ITM Syngas PDU**

Air Products will demonstrate the components of the ITM Syngas/ ITM H<sub>2</sub> technology in a laboratory Process Development Unit (PDU). The PDU will operate at an equivalent of 24,000 SCFD of syngas capacity, and will performance test sub-scale planar membranes under commercial process operating conditions.

### **Task 2.5: Nominal 500 MSCFD ITM Syngas SEP**

A Sub-scale Engineering Prototype (SEP) Unit will be constructed and used to demonstrate the ITM Syngas and ITM H<sub>2</sub> technology at up to an equivalent of 500,000 SCFD of syngas capacity. Initial work on the SEP project will proceed through scope definition and reactor vessel design and fabrication.

At the end of Phase 2, the projected commercial plant economics for ITM Syngas and ITM H<sub>2</sub> will be re-evaluated by Air Products, Chevron, McDermott and Norsk Hydro, based on the results from the PDU

and SEP operations. Three commercial-scale applications will be evaluated: hydrogen generation, offshore GTL, and remote Alaskan North Slope GTL.

Phase 3 (2 years) will demonstrate the production of syngas from an approximately 15 millions SCFD Pre-Commercial Technology Demonstration unit (PCTDU) using the ITM Syngas process.

**Engineering Development of Ceramic Membrane Reactor Systems for Converting Natural Gas to Hydrogen and Synthesis Gas for Liquid Transportation Fuels  
Air Products and Chemicals, Inc.**

Task Designation/Milestone	FY2002					2003
	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr4	Qtr 1
<b>Task 2.1: Evaluate Advanced Processes</b>						
Evaluate the ITM H <sub>2</sub> /ITM Syngas processes using PDU data			◆			
<b>Task 2.2: Evaluate ITM Materials and Seals</b>						
Select materials, catalysts and seals for SEP				◆		
Long-term stability tests of tubular membranes and seals at high pressure						◆
<b>Task 2.3: ITM Syngas Membrane &amp; Module Fabrication</b>						
Fabricate modules for additional PDU tests		◆				
Design SEP membrane modules			◆			
Commission the PDF				◆		
Initiate scale-up of membrane fabrication for SEP					◆	
<b>Task 2.4: Nominal 24 MSCFD ITM Syngas/ITM H<sub>2</sub> PDU</b>						
Performance test subscale modules in PDU		★				
Performance test second generation sub-scale modules in PDU						◆
<b>Task 2.5: Nominal 500 MSCFD ITM Syngas/ITM H<sub>2</sub> SEP</b>						
Define the scope of the SEP		◆				
Design the SEP reactor and initiate construction				◆		
Complete the SEP vessel fabrication						◆

FY2002 Begins October 1, 2001



★ = Critical Milestone



◆ = Milestone

## **Integrated Ceramic Membrane System for H<sub>2</sub> Production – Praxair, Inc.**

The ultimate goal of the program is to minimize the capital costs associated with small-scale hydrogen production system by reducing number of processing steps required to generate hydrogen. The proposed system will integrate mixed-conducting ceramic membrane technologies for the production of syngas (using oxygen transport membrane (OTM)) and hydrogen separation (using hydrogen transport membrane (HTM)). The HTM is a mixed conductor made up of ceramic material and is highly selective for hydrogen. The operating temperature required for hydrogen purification by HTM is similar to that required for syngas generation and offers excellent opportunity to integrate the two operations into one step.

Technical and economic feasibility evaluations for this concept has been completed. A decision to proceed to Phase II will be taken by the end of October 2001. The following is a preliminary outline of Phase II activities.

The main objectives of Phase II are to demonstrate the HTM reactor at bench-scale and to design hydrogen production system that is suitable for mass production. The following tasks will be carried out in FY 2002.

### **Task 1: HTM Materials Screening**

Various membrane materials will be screened for hydrogen separation. The material with high hydrogen flux, stability in the presence of syngas and low cost will be selected.

### **Task 2: Membrane Fabrication and Seal Development**

Based on the characteristics of the selected membrane, appropriate fabrication method will be developed to make the membrane elements. Seals will be developed that are stable under repeated thermal cycling.

### **Task 3: Design and Testing of a Bench-Scale HTM Reactor**

A bench-scale HTM reactor with multiple membrane elements will be designed and tested. Initial testing of the reactor will be carried out in hydrogen separation mode. Subsequently, water gas shift reaction and hydrogen separation will be carried out simultaneously.

**Integrated Ceramic Membrane System for Hydrogen Production  
Praxair, Inc.**

Task Designation/Milestone	2002					2003
	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4	Qtr 1
<b>Task 1: Membrane Material Selection</b>						
Measure hydrogen flux through different membranes			◆			
Test syngas tolerance of different membranes				◆		
Select membrane material				★		
<b>Task 2: Membrane Fabrication and Seal Development</b>						
Fabricate membrane elements					◆	
Test membrane seals						◆
<b>Task 3: Bench-Scale HTM Reactor Testing</b>						
Design Reactor						◆

FY2002 Begins October 1, 2001

★ = Critical Milestone

◆ = Milestone



## **Production of Hydrobromic Acid from Bromine and Methane for Hydrogen Production – SRT Group**

The effort will involve producing a prototype system based on the reaction between bromine and methane for the production of hydrobromic acid and the electrolysis of the acid back to hydrogen and bromine for a complete cycle. After a pre-commercial prototype reactor system is developed, the electrolyzer shall be replaced with a reversible fuel cell to enable energy storage.

The SRT process entails the reaction of bromine with methane to produce hydrogen bromide and carbon. The hydrogen bromide produced can be reacted with water to produce hydrobromic acid, which can be stored in a fiberglass tank or maintained as hydrogen bromide gas in a high-pressure stainless steel tank. Both chemicals can be electrolyzed for the production of  $H_{2(g)}$  and recovery of  $Br_{2(l)}$ . In this manner hydrogen is generated without greenhouse gas emissions.

SRT proposes to conduct the research to develop a bromine reformer, which reacts bromine liquid and natural gas in an exothermic reaction to produce hydrobromic acid. This reformer will be integrated with a 9 kW non-regenerative electrolyzer in a system using hydrobromic acid to allow for testing and modeling of the electrolyzer. Subsystem testing and development of the bromine tank, control system and ancillary systems are included. Included in this research effort is the investigation of the two storage concepts, as hydrogen bromide and hydrobromic acid. These two approaches will be analyzed for capital cost, safety, and process flexibility.

### **FY 2002 Task Descriptions**

#### **Task 3.0 Modeling**

SNL will provide a model to be used for design and analysis of the SRT system

#### **Task 4.0 Reactor Scale Up**

WRI will use the SNL model and fluid dynamics computations to scale the experimental reactor and its auxiliary systems to a working prototype that could be installed in an integrated system. The system will be used as a test bed to gather data required for the beta prototype where the electrolyzer will be replaced with a reversible fuel cell/electrolyzer. A 10kW laboratory electrolyzer presently owned by SRT will be used to gain experience and data. The prototype system will be capable of hydrogen production without energy storage. The system will be designed and tested to determine the effect of recycle, and by-product buildup. Subcontractor WRI will accomplish most of this task with input from SNL (funded separately) for data on kinetics and modeling of the reaction and reactor.

#### **Task 5.0 Analysis**

SRT, SNL and WRI will work collaboratively to analyze all of the data to calculate process efficiency of the reaction, determine the composition of the byproducts, evaluate the potential of cogeneration and validate the economics of the process.

#### **Task 6.0 CaO and SO<sub>2</sub> Reactions for SO<sub>2</sub> abatement**

SRT has performed preliminary calculations on the CaO and SO<sub>2</sub> reactions with bromine. Preliminary investigations and proof-of-principle experiments will be undertaken by SRT at the University of Florida at Gainesville. Reactants and products will be collected, analyzed and conversion rates will be determined.

**Production of Hydrobromic Acid From Bromine and Methane for Hydrogen Production  
SRT Group, Inc.**

Task Designation/Milestone	FY2002					2003
	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4	Qtr 1
Task 3.0: Modeling					◆	
Task 4.0: Bench Scale Testing						◆
Task 4.7: Assemble and operate Beta system				★		
Task 5.0: Analysis						◆
Task 6.0: SO <sub>2</sub> Abatement/Hydrogne Production Bench scale testing						◆

FY2002 Begins October 1, 2001



= Critical Milestone



= Milestone

## **BIOMASS-BASED PRODUCTION**

### **Fluidizable Catalysts for Hydrogen Production from Biomass Pyrolysis/Steam Reforming** **– National Renewable Energy Laboratory**

The goal of this project is to optimize a fluidizable particulate catalyst for the production of hydrogen from reforming pyrolysis oils.

Initial program work established that biomass pyrolysis oil could be steam-reformed to generate hydrogen using non-fluidizable (fixed-bed) commercial catalysts. These fixed-bed experiments showed that the carbohydrate-derived fraction of poplar pyrolysis oil could be almost stoichiometrically converted to hydrogen. However, process performance decreased with time because of char and coke deposition on the catalyst surface and in the bed itself thus limiting the reforming cycle to two or three hours. This cycle was even shorter when whole bio-oil or polymeric biomass-derived liquids (hemicellulose-rich fraction from biomass steam fractionation process) were used as feedstocks for hydrogen production.

Process performance was significantly improved by using a fluidized catalyst bed for reforming whole bio-oil and its fractions. The fluidized bed configuration, which provides better contact between the reactants and the catalyst, significantly extended time-on-stream. The reforming experiments conducted to date in the fluidized bed system with the carbohydrate-derived fraction of pyrolysis oils have shown promising results. The fluidized catalyst shows a slow decrease in activity with time, which NREL has shown can be reversed by catalyst regeneration, either on- or off-stream.

The mechanical strength of the fluidized catalyst is the last process issue that must be addressed. NREL has been using commercial reforming catalysts that are designed and used for fixed-bed applications. NREL made a fluidizable catalyst material by grinding the pelletized commercial catalysts and by screening out the desired particle size fraction. These particles show good catalytic activity but poor physical strength. The high attrition rate of the particles results in excessive losses of catalyst solids from the reactor. NREL is currently working on identifying commercial supports that can be made into fluidizable catalysts of required mechanical strength and attrition resistance for the fluid bed system. The next step and the focus of this proposed project is to develop a fluidizable catalyst, made from attrition resistant supports, that can be scaled up and used in an integrated fluid bed catalytic reformer with a pyrolysis reactor operating at a capacity of 10 kg/h of biomass.

Building on promising results, the focus of the proposed work is to refine support properties, design and produce reforming (Ni-based) catalysts from the best supports, evaluate performance for steam reforming pyrolysis oils to hydrogen, and characterize the best catalysts to better understand what factors improve performance. NREL will continue to work with Dr. Parent and Dr. Ritland (CoorsTek) and with CarboCeramics to provide appropriate supports and prepare catalysts. NREL also works with materials characterization staff (Basic Sciences and NCPV) to characterize the best supports and catalyst materials. NREL will continue to evaluate promising commercial catalysts as they become available.

#### **Task 1: Fluidizable Support Development**

This task focuses on further development of the CoorsTek attrition resistant alumina supports. NREL chose this material to work with because it consists of primarily alpha alumina of the right particle size (350  $\mu\text{m}$ ), is attrition resistant, and easily fluidizes. Because reforming rates have been shown to increase with increasing catalyst surface area in industrial fixed-bed reactors, the support surface area of the CoorsTek spherical aluminas needs to be increased. This work will be performed at CoorsTek by modifying the calcination temperature of green aluminas to develop increased surface area. CoorsTek recently increased the surface area of the Micro material to 0.2  $\text{m}^2/\text{g}$  with this method. The modified

materials will be tested at NREL for attrition as an inverse relationship between surface area and mechanical strength exists for most materials. When an optimum support is produced, NREL will then focus on adding gasification promoters to the support. Guidance on promoter composition and concentration is provided by earlier work performed by Garcia et al., 2000.

## Task 2: Catalyst Preparation and Optimization

NREL will use the best support developed in Task 1 to make several Ni-based reforming catalysts with variations in Ni content (1-15 wt %). The goal is to produce catalysts that retain attrition resistance and have improved activity and lifetime. NREL will use impregnation and solid mixing methods to add Ni to the supports. NREL will also look at the effect of adding promoters at this stage on performance. All catalysts will be tested for attrition and the best catalysts will move on to performance evaluation for reforming bio-oils to H<sub>2</sub>.

FY 2002 work will focus on developing the CoorsTek supports and producing catalysts from their best supports. FY 2003 work will focus on optimizing fluidization catalyst recipes for use in the pilot-scale integrated system and characterizing the best materials (before and after use) to develop an understanding of both catalyst production and subsequent process variables on catalyst performance.

Fluidizable Catalysts for Hydrogen Production from Biomass Pyrolysis/Steam Reforming NREL						
Task Designation/Milestone		FY2002				2003
	Qtr	Qtr 1	Qtr 2	Qtr 3	Qtr 4	Qtr 1
<b>Task 1: Fluidizable Support Development</b>						
Produce attrition-resistant alumina supports and develop an appropriate "recipe" for adding promoters during support preparation (for Task 2)			★			
<b>Task 2: Catalyst Preparation and Optimization</b>						
Develop a "recipe" for producing a range of robust promoted Ni fluidization catalysts					◆	

FY2002 Begins October 1, 2001      ★ = Critical Milestone      ◆ = Milestone

## **Biomass Pyrolysis for Hydrogen Production – Jet Propulsion Laboratory**

The topic of Jet Propulsion Laboratory's, (JPL), tasks for FY 02 were changed compared to what was provided at the 2001 Hydrogen Review Meeting according to directions from JPL's sponsors. This revised task constitutes the initiation of a diesel fuel reforming study. The long-term goal of this investigation is the quantitative prediction of the hydrogen yield from drops of an evaporating Diesel fuel spray in steam, leading to an optimization study for maximizing the hydrogen yield.

The physical configuration is as follows: a spray of Diesel fuel is injected into a chamber containing water steam, the fuel drops evaporate and the evaporated species reacts with the steam (steam reforming) to yield hydrogen and carbon dioxide. The generic, global chemical reaction is  $C_nH_m + 2nH_2O \rightarrow nCO_2 + (0.5m + 2n)H_2$ , and the interest is in maximizing the hydrogen yield. This will be a modeling and computational approach, as numerical simulations provide a financially economic way of process optimization when considering the influence of many parameters.

To ensure that the model is quantitative, two elements are necessary, as follows: (1) an appropriate spray model combining the turbulent behavior of drops and gas with the evaporative process, and (2) an appropriate reaction scheme and kinetic parameters portraying reforming. The focus of the FY02 activities is on the spray dynamics and evaporation. Two different topics will be addressed herein, both of them in the framework of Direct Numerical Simulations (DNS) with the goals of (i) creating a database from which to extract Subgrid Scale (SGS) models for further use in Large Eddy Simulations (LES) of turbulent sprays, and (ii) evaluate, in the laminar context, the ability of sprays with different cross-section injection geometry to disperse the drops and mix the evaporated species with the surrounding gas, so as to improve the reaction effectiveness. DNS are simulations whereby all scales of the flow are resolved, albeit for a domain much smaller than that of interest (due to the computational necessity of resolving all scales of turbulence – e.g. about  $10^8$  in each of the 3 directions - even for gaseous flows). These DNS are very computational intensive calculations whose sole purpose is the extraction of SGS models for use in LES, which are considerably less computationally intensive (by orders of magnitude). In DNS, the computational goal is the achievement of a transitional state (not fully turbulent, but having reached the threshold to turbulence), which serves as a basis for the extraction of SGS models that embed the essence of turbulence. The protocol is to use these SGS models in the LES equations, which are obtained by filtering the conservation equations so as to remove the small scales. Thus, in LES only the large scales of the flow are resolved and the small scales must be modeled. Credible SGS models for drop-laden flows with evaporation are not currently available. Therefore, JPL will initiate this study by first producing such models.

### **Task 1: Direct Numerical Simulations Consistent With Large Eddy Simulations**

The utilization of SGS derived models from DNS into LES is based on the combined assumptions of small (i.e. Kolmogorov) scale isotropy and similarity of SGS dependency on the resolved scale (i.e. LES) variables for transitional and fully turbulent regimes. These assumptions are inherent in the DNS/LES approach, but neither one of them is entirely established for gaseous, let alone general drop-laden flows. The small-scale isotropy is, in particular, dependent on the ratio of the Kolmogorov scale (the smallest turbulence scale) to the drop diameter. In this study, the drops being much smaller than the Kolmogorov scale, the issue of small-scale isotropy reduces to that for gaseous flows. The similarity of transitional and fully turbulent regime SGS dependency on the resolved scale variables is an issue that should be confronted in future comparisons between results from LES utilizing DNS-derived SGS models and equivalent experimental data.

However, a more pervasive assumption is also typically made in DNS of particle-laden flows targeting high temperature applications: the neglect of the diffusion velocity contribution in the heat flux, emulating modeling of flows with combustion. This assumption is not inherent in the DNS/LES approach, and can be evaluated using a DNS database. This evaluation is particularly important for DNS consistency since the initial gas temperature is chosen relatively low in DNS to insure that the drops

survive long enough to interact with the flow. Analysis of our previous databases reveals that at these low gas temperatures the diffusion velocity term magnitude rivals, and sometimes exceeds, the heat conduction term. Admittedly, this does not constitute proof of the importance of these terms because they were not included in the energy equation corresponding to the database; however, this is an indication that the assumption should be re-evaluated.

In principle, any SGS model derived from a DNS is physically correct only if this diffusion velocity term is included. This is true even if the SGS model is intended for use under high gas temperature conditions. Basically, the DNS equations should be self consistent for the conditions of the DNS regime, and the projected applicability of DNS derived results to fully developed turbulent flow should be left as a hypothesis standing on its own, and unburdened by other assumptions.

To obtain new databases (representing transitional states) including the diffusion velocity contribution to the heat flux, a new set of simulations will be here conducted by including this term in the energy equation of our previous studies. The configuration will be the same as in our previous studies (i.e. temporal shear layer), and transitional states will be obtained for 3 simulations: two simulations having the same initial Reynolds number but different mass loadings (the mass loading is the total mass of the drops divided by the total mass of the gas), and two simulations having the same mass loading but different initial Reynolds numbers. These databases will be analyzed at different physical times including the final simulation time, and the budget of the energy equation will be evaluated thereby assessing the validity of neglecting the diffusion velocity contribution.

The databases created above will be further used to evaluate the contributions of various physical mechanisms to the small-scale gaseous dissipation, which is the quantity that must be reproduced by the SGS. To undertake this study, JPL will first derive the entropy equation for the gas in the context of a drop-laden gaseous flow. The dissipation is in fact the irreversible entropy production, and it can be evaluated from the DNS database using the appropriate terms of the entropy equation developed herein. By calculating the filtered dissipation and taking the difference between the unfiltered and filtered values, one obtains the dissipation associated with the small scales of the flow. The irreversible entropy production generally contains gas-boundary-generated terms, viscous dissipation terms, heat dissipation terms and species (i.e. scalar) dissipation terms. The gas-boundary-generated terms are those associated with the source terms in the conservation equations, as each real (i.e. DNS) drop boundary constitutes a boundary for the gas phase. Indeed, each drop represents a source/sink for the gaseous flow for the mass (due to evaporation), for momentum (due to drag and evaporation) and for energy (due to evaporation, drop heat up, kinetic energy of the evaporated gas and drag). With increasing mass loading, the contribution of these source terms will become increasingly important.

It is noteworthy that in many gaseous flows, the local dissipation is not well predicted by the SGS, especially if the model is of the Smagorinsky (SM) type. For example, a notorious situation falling in this category is the application of the constant-coefficient SM model to conditions where the strain rate and stress might not be locally aligned, such as in recirculating flows prevailing in sprays injected in enclosed chambers. In fact, the SM coefficient has been found to depend on the flow field, with different values for isotropic turbulence, channel flows and mixing layers. Although the lack of local correlation between some models and SGS fluxes is intellectually disturbing, in some gaseous flow LES calculations this deficiency may not be essential. In contrast, in drop-laden flows, because the source terms are locally produced, and because they may represent the highest small-scale dissipative contribution, the prediction of the local dissipation may become a very important goal. This is precisely what will be determined herein. JPL notes that there is already evidence that LES results are highly dependent on the modeling of the source terms. For example, some investigators must assume that drops below an arbitrary size must instantaneously evaporate in order to obtain agreement between simulations and data; such an assumption is ad-hoc because the threshold drop size will change with the flow geometry and other conditions. Despite this LES sensitivity to the source term model, the modeling of the source terms has never been addressed from first principles. This is, however, of crucial importance to the reforming of the evaporated hydrocarbons because this is precisely what will be participating in the reforming reactions.

Specifically, in this task JPL will: (i) conduct 3 DNS to achieve transitional states, (ii) analyze the transitional databases to determine the contribution of each term to the energy budget, (iii) derive the entropy equation for a flow laden with drops to analyze the database and determine which terms are most important for reproducing the dissipation, and thus which SGS terms must be accurately modeled. Since these simulations will be very computationally intensive, to reduce the computational burden, they will be performed with decane instead of Diesel fuel, as decane is a single component species having properties close to Diesel fuel.

### **Task 2: Effect of Different Cross-Section Spray-Injection Geometries**

In parallel with TASK 1, and foreseeing our ultimate goal of optimizing hydrogen production from Diesel spray reforming, JPL will investigate several cross-section injection geometries (circular, square, rectangular, ellipsoidal and triangular) for gaseous jets laden with drops to determine if there is a particular geometry that is more beneficial to drop dispersion and mixing of the evaporated species with the gaseous surroundings. For gaseous jets, there is already experimental as well as numerical evidence that jets with non-circular inlet geometries display superior entrainment and mixing characteristics. However, JPL is not aware of equivalent studies for drop-laden jets, i.e. sprays.

Therefore, JPL will conduct a DNS investigation in the context of laminar sprays to determine if the advantages observed for gaseous jets are translatable to evaporating sprays. Specifically, for each of the above-stated geometries, JPL will conduct simulations for both gaseous and drop-laden jets and compare the results (i) between gaseous and drop-laden jets having the same injection geometry, and (2) among the different drop-laden jet geometries. The results should indicate which are the best candidate geometries to be simulated when the SGS models will be ready to be inserted into LES.

**Biomass Pyrolysis for Hydrogen  
Jet Propulsion Laboratory**

Task Designation/Milestone		FY2002				2003
		Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4
<b>Task 1: Direct Numerical Simulations Consistent with Large Eddie Simulations</b>						
1. 3-dimensional computer simulations of a drop-laden mixing layer for the purpose of generating transitional states					◆	
2. Derivation of the entropy equation		◆				
3. Analysis of the database					★	
<b>Task 2: Effect of Different Cross-Section Spray-Injection Geometries</b>						
1. Transformation of the shear layer code into a spray code (gaseous jet with evaporating drops)			◆			
2. Simulations of single and two phase jets with circular injection geometry for laminar situations				◆		
3. Simulations of single and two phase jets with elliptic, square, rectangular and triangular injection for laminar situations						◆

FY2002 Begins October 1, 2001



= Critical Milestone



= Milestone



## **Supercritical Water Partial Oxidation – General Atomics**

General Atomics, together with World-wide Environmental Energy Systems Inc. (wwEESI) and Combustion Systems, Inc. (CSI) are developing an advanced power generating system based on Supercritical Water (SCW) technology. Supercritical Water Partial Oxidation (SWPO) is a new technology for efficient and environmentally attractive gasification and hydrogen production from low-grade fuels such as biomass, municipal/solid waste (MSW) and high-sulfur coal.

SWPO involves carrying out oxidative reactions in the SCW environment – akin to high-pressure steam – in the presence of sub-stoichiometric quantities of oxidant, typically pure oxygen or air. The key advantage of the proposed SWPO process is the use of partial oxidation in-situ to rapidly heat the gasification medium, resulting in less char formation and improved hydrogen yield. Another major advantage is that the high-pressure, high-density aqueous environment is ideal for reacting and gasifying organics. The high water content of the medium encourages formation of hydrogen and hydrogen-rich products and is highly compatible with high water content feeds such as biomass materials. By the same token, the high water content of the medium is effective for gasification of hydrogen-poor materials such as coal.

The pressurized nature of the SWPO process naturally lends itself to the liquefaction and sequestration of CO<sub>2</sub>. The combination of high pressure and the cold sink available with a liquid oxygen oxidant enables ready liquefaction of CO<sub>2</sub>. It may then be recycled, injected for oil recovery or otherwise handled to reduce greenhouse effects.

The principal tasks composing the current Phase I activities are summarized below.

### **PHASE I (FY-2001):**

#### **Task 1: Bench-Scale Testing/Feasibility**

#### **Task 2: Pilot-Scale Design & Analysis**

#### **Task 3: Development Plan**

The second phase of the SWPO technology development is a 2-year phase involving design, construction and optimization testing of a pilot-scale reactor. For this plan we have broken in two sub-phases, A and B, corresponding to the NREL Hydrogen Program annual planning cycle. The portion of this phase corresponding to FY-2002 is identified as Phase IIA.

### **PHASE IIA - PILOT-SCALE REACTOR DEVELOPMENT (FY-2002):**

#### **Task 1: Engineering & Detailed Design of Pilot-Scale SWPO Reactor**

In Task 1, a pilot-scale reactor will be engineered and designed based on the information acquired during the Phase I testing. GA will prepare engineering drawings and specifications appropriate for reactor fabrication.

#### **Task 2: Fabricate, Install, Checkout & Systematize Pilot-Scale Reactor**

The pilot-scale reactor will be fabricated in accordance with a GA prepared procurement package. The fabricated reactor will be installed in the GA pilot-test facility and configured for SWPO operation. The reactor will be checked-out and operated in the test facility system until successful systematized.

**Task 3: Develop Reactor Optimization Test Plan For Phase IIB**

GA will develop a test plan designed to systematically and thoroughly explore the process parameters critical for optimization of operating conditions and hydrogen yields from the SWPO reactor. This test plan will provide the basis for the Phase IIB optimization testing.

**PHASE IIB – REACTOR PERFORMANCE OPTIMIZATION & EVALUATION (FY-2003):****Task 1: Perform Parametric Reactor Optimization Tests****Task 2: Engineering Evaluation of Data For Demonstration Plant Scale-Up****Task 3: Update SWPO Development Plan**

Supercritical Water Partial Oxidation General Atomics						
Task Designation/Milestone	FY2002					2003
	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4	Qtr 1
<u>Phase I</u>						
<b>Bench-scale testing</b>		◆				
<b>Pilot-scale Design</b>		◆				
<b>SWPO Development Plan</b>		◆				
<u>Phase IIA</u>						
<b>Engineering Design Pilot-scale Reactor</b>						
Engineering Design			◆			
Detail Design Docs.				◆		
<b>Fabricate, Install, Checkout &amp; Systematize Pilot-Scale Reactor</b>						
Procure & Fabricate Reactor						★
Install, Checkout & Systemitize Reactor						◆
<b>Optimization Test Plan</b>						◆

FY2002 Begins October 1, 2001      ★ = Critical Milestone      ◆ = Milestone

## **Biohydrogen Production from Renewable Organic Wastes – Iowa State University**

For global environmental considerations, production of hydrogen by biological reactions from renewable organic waste sources represents an important area of bioenergy production. Many investigations have been conducted using pure cultures of hydrogen-producing bacteria. Some of the studies showed promising results. However, since wastewater is contaminated by bacteria, the purity of any wastewater treatment reactor is lost and therefore the treatment of wastewater has to be a mixed culture process. Moreover, these studies were limited to the basic studies on microbial hydrogen metabolism. Their viability to real processes in terms of technical feasibility and commercialization potential has not been evaluated.

The goal of this project is to develop an anaerobic fermentation process that converts negative value organic wastes into hydrogen-rich gas that can significantly enhance the economic viability of many processes either by utilizing hydrogen as a fuel source or as raw material for industries that consume hydrogen. This project will contribute to the advancement of DOE's goals "produce hydrogen from renewable energy resources at a cost of \$10 - \$15 per million BTU for direct renewable systems without significant carbon dioxide emissions."

### **Task 2: Microbial Community Characterization (Subcontract at University of Illinois)**

This task is to identify and quantify hydrogen-producing populations in bioreactors operated for biological hydrogen production from renewable organic waste streams and relate this information to process optimization.

The microbial communities in Iowa State University's (ISU) bioreactors will be examined using three different, but interrelated approaches. First, a recently developed nucleic acid based "fingerprinting" method (terminal restriction fragment length polymorphism; T-RFLP) will be used to identify the most abundant populations in their bioreactors. T-RFLP is a technique used to evaluate the diversity of complex microbial communities. Second, T-RFLP with PCR primers specific for hydrogen-producing populations (belonging to important genera identified in the first step) will be used to determine the presence and diversity of species within these genera. Using a technique recently developed by Moon and Sanford (personal communication), ISU will be able to sequence the 16S rDNA corresponding to the bands of interest in the T-RFLP electropherograms to confirm the identity of important populations. Finally, rRNA-targeted oligonucleotide hybridization probes will be used to determine the abundance of important populations at various levels of specificity.

The information obtained from these three approaches will be used to determine the phylogenetic position of new (if any) hydrogen-producing bacteria and to design new, more specific oligonucleotide probes. These new probes can then be used to determine the abundance and activity of various hydrogen-producing bacteria in the bioreactors. This process should identify the organisms responsible for hydrogen production in our bioreactors. Changes in microbial community structure will continue to be monitored in the bioreactors as operational changes are made.

### **Task 3: Process Optimization of Continuous-flow Reactors**

The ultimate goal of the project is to develop a commercial scale application. It relies on the success of the continuous-flow operation. This task is an on going task that started in the 4<sup>th</sup> quarter of the first year. Two lab-scale bioreactors are operated as completely stirred tank reactors (CSTRs). They are operated at different organic loading rates by controlling the hydraulic retention time (HRT) with the optimal pH, temperature, and oxidation-reduction potential determined in the previous steps. The F/M ratio, an important parameter, will also be manipulated by wastage of sludge from the reactors at regular intervals. The mixer rpm will be controlled at the optimum velocity for immediate removal of the produced

hydrogen gas from the system. The experience from this study will provide valuable information to establish design criteria for a pilot-scale reactor degrading real wastes.

A recent important discovery of a reactivation chamber can greatly improve the process stability and hydrogen yield. An Intellectual Property Disclosure based on the discovery was filed to the Iowa State University Office of Intellectual Property and Technology Transfer in March 2001. This task is also designed to conduct a series of tests on the reactivation chamber concept. An experimental protocol designed to evaluate the operating parameters of the reactivation chamber is incorporated into the task.

#### **Task 4: Investigation of H<sub>2</sub> Production Potential of Different Wastewaters**

Batch experiments using serum bottles will be conducted to test the hydrogen production potential of different wastes. This will provide a preliminary assessment of the hydrogen production potential of the various waste streams. The results from this task will assist in the selection of potential target waste streams for the production of hydrogen. An anaerobic respirometer equipped with an automatic data acquisition system will be used in this phase of the study. This respirometer consists of a set of biological reaction vessels and a gas measuring base unit which is capable of determining the biogas production rate in a controlled environment over a short period of time. The microflora isolated during the previous tasks will be used as inoculum for this stage. The waste streams tested during this stage will be first characterized to determine their compositions in terms of carbohydrate, protein, and fat contents. The waste streams studied will include food processing wastewater (potato and whey), agricultural residuals such as corn stalks, municipal wastes, industrial wastes, pulp and paper wastes, and meat packing wastes supplied by EcoFuel, Corp. and Smithfield Foods, Inc.

The objective of this task is to develop a common correlation between hydrogen production potential and the waste composition. Furthermore, suitable waste stream for biohydrogen production can be identified.

#### **Task 5: Pilot Test of Selected Waste Streams**

Reactor sizing and operating parameters from the successful completion of task 3 and appropriate waste streams identified from task 4 will be used to construct and run a pilot-scale unit. The pilot scale testing will be conducted at the Biomass Energy Conversion Center of Iowa Energy Center.

<b>Biohydrogen Production from Renewable Organic Wastes</b> <b>Iowa State University</b>						
Task Designation/Milestone		2002				2003
	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4	Qtr 1
<b>Task 2: Microbial Community Characterization</b>						
Development of quantification methods		◆				
Population data collection and analysis					◆	
<b>Task 3: Optimization of Continuous-flow Reactors</b>						
Testing for operating parameters	◆					
Testing for different activation chambers			◆			
<b>Task 4: Investigation of H<sub>2</sub> Production Potential of Different Wastewaters</b>						
Testing for real wastes in continuous reactors				★		
<b>Task 5: Pilot Test of Selected Waste Streams</b>						
Design a pilot testing unit						◆
FY 2002 Begins October 1, 2001    ★ = Key Milestone      = Milestone						

## **Bio-production of Hydrogen Using Thermophilic Bacteria – National Energy Technology Laboratory**

Significant amounts of hydrogen gas can now be produced on demand as a byproduct of the catabolism of thermophilic bacteria. This approach holds promise of producing hydrogen cost-effectively while requiring development of only a comparatively modest infrastructure to actually produce the hydrogen.

Most of the experiments at the National Energy Technology Laboratory (NETL) have been conducted in small batch reactors. However, preliminary tests using a Continuous Stirred Tank Reactor (CSTR) shows a consistent generation of about 5 liters of gas in 12 hours, containing more than 21% hydrogen. A CSTR volume of about 2 liters was used, giving a calculated hydrogen generation rate of about 43ml/l-hour. Additionally, NETL has recorded generation of concentrations of more than 34% hydrogen gas from both CSTR and batch mode reactors with no apparent inhibition or toxicity to the bacteria. This is a very robust process for production of hydrogen and all indications at this time suggest that this process has the potential for scale-up to a continuous hydrogen-generating process.

### **Tasks:**

NETL's original plans were to move forward aggressively to scale up the bioprocess they have developed. However, the project reviewers consider their results "so remarkable" that they are rearranging their task priorities to further verify "revolutionary" findings presented during the FY2001 Annual Hydrogen Review.

#### **Task 1: Continue efforts to define the mode of metabolism used by these organisms to break down (catabolize and use) carbon sources during the production of hydrogen**

This is a very fundamental question, and the answer to this question will provide an important indication of the underlying efficiency of the process. NETL's hypothesis, based on a great deal of evidence, is that this is a respiratory process. If this hypothesis is proven correct, they can then anticipate obtaining very high hydrogen production efficiencies. A respiratory process can approach 100% efficiency, while a fermentative process is only calculated to be 20-30% efficient. To thoroughly examine this hypothesis, NETL plans to conduct very precise analyses using a liquid chromatograph-mass spectrometer to examine the liquid precursors and products, and analyses of gases utilized and produced using an existing magnetic sector mass spectrometer. It is well established in the literature that the end products of fermentation include one or more of the following: ethanol, acetate, lactate, alanine. At the very least, NETL will be looking to identify these compounds within liquid media that has been utilized by bacteria to produce hydrogen. In addition, they anticipate continued exploration of the role of oxygen relative to hydrogen production. Dissection of the putative role of oxygen in this process will be conducted using stable isotopes of oxygen and determining where the stable isotope is found following catabolism of appropriate carbon sources and generation of hydrogen.

#### **Task 2: Complete assembly of scale-up of CSTR apparatus and integration with ancillary analytical tools**

To date, NETL has obtained and tested most of the components needed for continuous monitoring by their CSTRs. As each of the individual components are tested and proven to provide accurate results, that system will be integrated with the CSTR and the New Brunswick Biocommand™ software. This will require considerable time, expertise, and the skills of additional highly trained personnel.

Once all of the components of NETL's system are on-line and have been integrated with the CSTR, they will begin comprehensive testing to answer a number of questions that can only be answered using a CSTR. Questions such as:

- a. What degree of efficiency can be anticipated when cultures of these organisms are maintained at steady state?
- b. What are the maximum yields of these organisms?

- c. What is the true rate of hydrogen production by a given population of these organisms?
- d. Is increase in biomass (log phase growth) required for hydrogen production, or can this process be decoupled from biomass increases?
- e. Can these organisms also “fix” (and utilize) molecular nitrogen from the gaseous phase?

**Task 3: Screen hydrogen producing species of the order *Thermotogales* to determine the variety of carbon sources each can use, and determine maximum hydrogen production**

NETL is currently standardizing Biolog™ plates to conduct a rapid screening program to determine how wide a variety of different carbon sources can be used by the various members of the order *Thermotogales*. Once food preferences for any given member of this order are established, NETL will conduct batch experiments to match and optimize the medium and carbon sources for each high performing strain relative to hydrogen production. To date they have already discovered three different species in two different genera of the order *Thermotogales* that produce over 30% hydrogen gas in batch experiments.

<b>Bio-production of Hydrogen using Thermophilic Bacteria</b> <b>National Energy Technology Laboratory</b>						
Task Designation/Milestone		FY2002				2003
	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4	Qtr 1
<b>Task 1: Define mode of thermophilic metabolism</b>			◆			
Attempt to find fermentation products	◆					
Track path of isotopic oxygen during catabolism						◆
<b>Task 2: Complete assembly of CSTR system</b>		★				
Complete shake-down of combined system			◆			
Begin collection of data from scale-up system				◆		
Define continuous hydrogen generation needs		◆				
Begin calculation of efficiency and rate		◆				
<b>Task 3: Screen all species for carbohydrate utilization</b>					◆	
Test species with carbon sources utilized						◆
Find best hydrogen/carbon source (by species)						◆

FY2002 Begins October 1, 2001      ★ = Critical Milestone      ◆ = Milestone

## **Hydrogen from Post-Consumer Wastes – National Renewable Energy Laboratory**

The goal of the proposed project is to develop a robust small-to-medium capacity, thermo-catalytic process for producing hydrogen from readily available post-consumer materials. Such process could be applied following a distributed hydrogen production strategy.

Demonstrate feasibility of the production of hydrogen from synthetic polymers and from waste grease with a yield of 80% of the stoichiometric potential.

At present, the commercial production of hydrogen is essentially carried out by catalytic steam reforming of hydrocarbons: natural gas and naphtha. Because of the rapidly rising costs of natural gas the use of other raw materials becomes increasingly attractive. This research concept proposes to develop a technology for producing hydrogen from two types of waste post-consumer materials: plastics and “trap” grease.

Plastics, especially polyolefins, have significant potential but are not yet used as a resource for hydrogen production. Plastics account for 8-9% of today’s waste stream, or about 30 billion pounds annually, that are mostly landfilled. Potentially, the waste plastics could be used to generate 12 billion pounds of hydrogen per year.

Waste grease is largely available throughout the country. It is recovered from two main sources: traps installed in the sewage lines of restaurants and food processing plants (from which it is pumped into trucks) and wastewater treatment plants, where it flows through municipal sewage systems. So far, this material has not found any economically viable application and is mostly disposed of; for example, grease trap-pumping companies in the Boston area discharge pump trucks at processing facilities that charge tipping fees of 11¢/gallon. The average amount of the recovered waste grease is 13 lbs/person/year, which has the potential for producing annually 1 billion pounds (0.5 Mtonnes/year) of hydrogen.

If successful, this strategy would: save natural gas, generate regional industries, and substantially reduce the waste stream, adding environmental benefit to the proposed process. A strategy similar to that applied in the Biomass-to-Hydrogen project could be developed where targeted waste streams, such as those from manufacturing could be converted to higher-value products with the residues of the operation used for producing hydrogen. Such an approach could improve the process economics and speed deployment.

The challenge is to efficiently convert these plastic polymers and the constitutive molecules of trap grease (predominantly free fatty acids and triglycerides) to hydrogen at a similar cost to that for the existing natural gas-based technologies. We believe that such a challenge can be met by a combination of an appropriate technology and a low-cost feedstock.

### **Task 1: Pyrolysis/reforming and partial oxidation/reforming tests using selected plastics**

Small-scale experiments on selected plastics (polyolefines) and composites will be carried out using a reactor interfaced with the molecular-beam mass-spectrometer (MBMS). Both two-step (pyrolysis followed by reforming) and one-step (catalytic pyrolysis) processes will be tested. Production of hydrogen will be studied as a function of pyrolysis and reforming process parameters such as temperatures, catalyst (commercial and research catalysts will be employed), and space velocity. These initial tests will allow us to determine appropriate process conditions for bench-scale experiments. Mechanistic understanding will also be gained because of the uniqueness and depth of the MBMS technique.



**Task 2: Bench-scale tests of catalytic reforming of waste grease and glycerol fraction**

Tests of catalytic reforming of whole waste grease and of glycerol fraction generated in a bio-diesel plant will be carried out using the bench-scale fluidized bed reactor system to produce hydrogen. Different conditions will be studied to demonstrate a long-duration process performance. It is especially important to evaluate the influence of the inorganic impurities on the catalyst life time. If necessary, pretreatment of the grease and of the glycerol will be employed to remove the contaminants that poison the catalyst.

**Task 3: Bench-scale pyrolysis/reforming system for producing hydrogen from plastics**

The bench-scale fluidized bed system will be modified to allow us for the integrated pyrolysis/reforming operation. Pyrolysis reactor supplied with a solid feeding system will be constructed to generate hydrocarbons from plastics. These hydrocarbons will be fed to the existing reformer to produce hydrogen. The bench-scale tests that will be carried out in the next fiscal year will validate the process concept (product gas collection, mass balances, catalyst performances).

Hydrogen from Post-consumer Wastes NREL						
Task Designation/Milestone	FY2002					2003
	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4	Qtr 1
<b>Task 1: Pyrolysis/reforming and partial oxidation/reforming tests using selected plastics</b>						
Demonstrate the process concept; at the small-scale achieve 80% of the theoretically possible conversion of plastics to hydrogen					◆	
<b>Task 2: Bench-scale tests of catalytic reforming of waste grease and glycerol fraction</b>						
Demonstrate long duration performance (200 hours on stream) of the catalyst during steam reforming of waste grease			◆			
<b>Task 3: Bench-scale pyrolysis/reforming system for producing hydrogen from plastics</b>						
Construct a bench-scale two-step pyrolysis/reforming system					★	

FY2002 Begins October 1, 2001      ★ = Critical Milestone      ◆ = Milestone

## **Biological H<sub>2</sub> from Fuel Gases and from Water – National Renewable Energy Laboratory**

The goal of this project is to utilize unique photosynthetic microbes to quantitatively shift and condition a crude synthesis gas from thermally gasified biomass into H<sub>2</sub>-rich gas stream. This goal will be accomplished by examining the microbial water-gas shift reaction at physiological, biochemical, and genetic levels to understand its regulation, the components involved, and the rate-limiting step(s) in order to enhance overall activities and durability of this process.

There are several near-term objectives for FY02:

- Gain fundamental understanding of how the pathway of CO to H<sub>2</sub> is regulated by the presence of CO, and at what levels, during growth in order to maximally maintain its activity and durability.
- Complete the characterization of O<sub>2</sub>-tolerant hydrogenase and submit a manuscript to a peer-review journal documenting the results.
- Perform preliminary work on the genetic system of *Rubrivivax gelatinosus* CBS-2 allowing for the cloning of the hydrogenase gene and the identification of related proteins necessary for the water-gas shift reaction.

Previous data indicates that upon adding 17% CO to the gas phase of a un-induced photosynthetic culture, H<sub>2</sub> was detected within four to five hours in the light. The induction kinetics shows a rapid appearance of the CO shift activity during the first day with high rates, followed by a lower but constant steady-state level of the CO shift activity for the next two days. It is not clear why there is an initial burst of activity. It was also observed that when a fresh medium was inoculated with cells previously induced with shift activity, the resulted culture has less shift activity upon feeding CO, in comparison with a fresh medium inoculated with an un-induced culture. One logical explanation is that CO also regulates the overall shift rates. Previous data indicated that when hydrogenase was completely purified from CODH, the hydrogenase actually becomes extremely sensitive to CO, exhibiting a  $K_i$  of 3.5  $\mu$ M CO, the concentration that inhibits 50% of the hydrogenase activity. This finding is consistent with reports in literature that CO is a potent inhibitor to most hydrogenase enzymes (Adams *et al.*, 1981). Carbon monoxide therefore plays multiple roles in the microbial CO oxidation system; it serves as a substrate, as an inducer, and an inhibitor. Consequently, in order to sustain optimal activity, NREL must understand the role CO plays and seek a balance between CO concentration in the gas phase versus proper cell density for maximal induction. NREL proposes to examine, in detail, if various levels of CO would affect the extent of induction initially, and whether CO, and at what concentration, has to be present throughout to ensure the durability of the shift activity.

The second approach to gain insight into the regulation and components involved is via molecular biology to understand the genetic system of the CO shift pathway. This technique has several advantages, one being that even though most anaerobic enzymes are very labile; genes coding for them are stable and easier to manipulate. The other benefit is that genes of related function are usually clustered adjacent to each other on DNA. Gene sequences for CO-linked hydrogenase and related proteins from *Rs. rubrum* have been published (Fox *et al.*, 1996). Specific probes and primers can be designed based on sequence homology. By hybridizing the probes with digested DNA fragments from CBS-2, hydrogenase gene can be identified. Cloning the hydrogenase gene permits its amplification resulting in over-expression of its activity. Since genes of related function are clustered together on DNA, examination of the adjacent open reading frames will reveal information as to what other components are involved or co-induced during culturing in CO. Comparing their sequence homology with data in Gene Bank would allow for the prediction of the nature of these proteins. It is highly likely that one of them is a transcriptional activator. If manifested, it can be manipulated such that CO shift pathway is synthesized constitutively.

**Task 1: Physiological/Biochemical Study of the CO Shift Reaction**

This task will examine, in detail, the following parameters in inducing and regulating the overall CO shift activity: (a) Optimal amounts of CO in inducing the shift activity initially, NREL will determine the kinetics of induction for each CO levels; (b) Once the shift pathway is fully induced, NREL will determine the longevity of the activity without re-feeding CO. Without an inducer present, cells will not transcribe new proteins. This will yield information as to how long the pre-existing proteins will last and also how often CO has to be supplemented; and (c) Effect of adding CO to a culture that has been depleted of CO. A transcription inhibitor such as chloramphenicol will be added along with CO to determine if any enhanced activity is due to new protein synthesis or simply an activation of the existing proteins. (d) How cellular oxidation-reduction level would affect the induction, rates, and longevity of the shift reaction. For all the above experiments, NREL will perform rate measurements of overall activity (CO to H<sub>2</sub>), CODH (CO to methyl viologen reduction), and hydrogenase only (use dithionite-reduced methyl viologen) and determine which step is controlled by CO addition or depletion.

The work to characterize O<sub>2</sub> tolerance of the CO-linked hydrogenase is near complete. Using a kinetic H<sub>2</sub>-D<sub>2</sub>O (H-D) exchange assay developed at NREL, it has been established that hydrogenase in whole cells can function partially with the simultaneous presence of O<sub>2</sub>. Similar assays need to be performed using purified hydrogenase instead to avoid complications from the competing uptake hydrogenase. NREL will continue with the purification of the CO-linked hydrogenase to yield enough quantity and of high purity to perform this assay. Once complete, a manuscript will be prepared and submitted to a peer-review journal documenting O<sub>2</sub> tolerance of this unique hydrogenase.

**Task 2: Molecular biology of the hydrogenase in the CO Shift Reaction**

This task will perform preliminary work on the genetic system of the CO-oxidation pathway in *Rx. gelatinosus* CBS-2. Gary Vanzin, a newhire molecular biologist postdoc, will perform the bulk of this task. CBS-2 is a new isolate and little is known about its genetic system. NREL will (a) compare various restriction enzymes in rates and completeness of digesting CBS-2 DNA into sizes suitable for chromatography. (b) perform Southern blotting and hybridization experiments. Based on sequence homology with the hydrogenase from *Rs. rubrum*, NREL will design primer and use PCR technique to generate probe specific for the hydrogenase from CBS-2. The probe will be hybridized with the CBS-2 DNA to locate the hydrogenase gene. Primers and probes for CODH and its cofactor from *Rs. rubrum* can be designed similarly also to identify related genes in the CO shift pathway of CBS-2. (c) construct a bookshelf and genomic DNA libraries. Bookshelf library can be constructed using only those DNA fragments hybridized with the probe while genomic library would use total digested DNA. Bookshelf library has a good chance of success since it has already ruled out most non-specific genes. (d) both the bookshelf and the genomic DNA libraries will be screened for those recombinant clones containing the hydrogenase gene. Those clones will be harvested, amplified with PCR and sequenced to identify the hydrogenase gene.

**Biological Hydrogen from Fuel Gases and from Water  
National Renewable Energy Laboratory**

Task Designation/Milestone		FY2002					2003
		Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4	Qtr 1
<b>Task 1: Physiological/Biochemical Study of the CO Shift Reaction</b>							
Complete the investigation of effects of CO and nature of the inoculant on the maximal induction and maintenance of the shift activity						★	
<b>Task 2: Molecular biology of the hydrogenase in the CO Shift Reaction</b>							
Design primer and probe, and successfully hybridize hydrogenase gene of <i>Rx gelatinosus</i> CBS-2						◆	

FY2002 Begins October 1, 2001

★ = Critical Milestone

◆ = Milestone

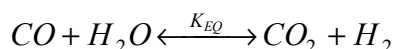
## **Bioreactor Development for Biological H<sub>2</sub> Production – National Renewable Energy Laboratory**

The goals of this project are to develop bioreactors with enhanced mass transfer capabilities that will promote an economic biological conditioning of fuel gases, and to demonstrate the water-gas shift reaction on synthesis gas produced from biomass gasification.

The project objectives for FY 2002 are:

- Design, construct, and operate a bioreactor capable of operating at system pressures of 10 atm
- Measure the specific carbon monoxide shift kinetics of the photosynthetic bacterium *Rubrivivax gelatinosus* CBS2

The biologically mediated water-gas shift reaction may be a cost-effective technology for the conditioning of synthesis gas. NREL researchers have isolated a number of photosynthetic bacteria that can perform the water-gas shift reaction, in which carbon monoxide is oxidized to carbon dioxide while simultaneously water is reduced to hydrogen. The overall stoichiometry of this reversible reaction is:



One significant advantage to using bacteria to perform the water-gas shift reaction is their ability to operate at ambient temperature. Because the reaction occurs at ambient temperature, the reaction is not equilibrium-limited (at 25°C,  $K_{EQ} \sim 5 \times 10^4$ ). The advantages of low operating temperature and lack of equilibrium limitation make the biological shift reaction a promising alternative to conventional shift technologies. Preliminary data already collected at NREL suggest that this reaction is far more rapid than the rate at which CO can be supplied to the bacterial culture. This is consistent with many other gas/liquid biological reaction systems, including most aerobic fermentations, where metabolic rates are commonly limited by the transfer rate of a gaseous substrate to the liquid media.

In the coming year, NREL proposes to continue this work, again concentrating on two related tasks: the investigation of a promising new reactor design, and the measurement of the intrinsic shift kinetics of the photosynthetic bacterium *Rubrivivax gelatinosus* CBS2.

### **Task 1: Investigate Pressurized Bioshift Reactors**

The scale-up experiments NREL performed during FY01 and the associated reactor modeling work, clearly show that the transfer of CO from the gas phase to the bacteria-laden liquid phase limits the overall H<sub>2</sub> production rate. One solution to such mass transfer limitations is to increase the system pressure, since higher pressures will lead directly to higher mass transfer rates, which in turn should lead to higher volumetric productivities (i.e., higher rates of CO shifted per reactor volume). In theory, a tenfold increase in system pressure should lead to a tenfold increase in reactor productivity. In addition, a number of potential applications for the bioshift technology involve CO-containing gas streams that will be available at elevated pressures (5-15 atm), so a reactor operating at such pressures will be a requirement for such processes.

Admittedly, the operation of a pressurized reactor utilizing a toxic gas such as CO (and generating an explosive gas such as H<sub>2</sub>) will be more difficult than operating a similar-size ambient pressure reactor. However, in FY02, we will address these challenges and design, build, and operate a pressurized bioshift reactor.

## Task 2: Measuring the Intrinsic CO Shift Rate of *Rubrivivax gelatinosus* CBS2

NREL began work in FY01 to determine the intrinsic CO shift rate of *R. gelatinosus* CBS2. The “intrinsic rate” is defined as the rate of CO uptake (and subsequent H<sub>2</sub> production) per unit mass of the bacterium in the absence of any mass transfer limitations. This fundamental information is critical because it sets the maximum possible volumetric productivity of a bioshift reactor employing this microorganism. That is, if a bioshift reactor can be developed with no mass transfer limitations, its maximum rate will be controlled by the microorganism’s intrinsic activity.

In FY01 NREL adopted a promising experimental protocol from the literature, and this work is progressing. However, NREL has found that the measured intrinsic CO shift rate is very sensitive to experimental parameters, and they have not yet completed this measurement. In FY02 NREL will complete this work, and determine the intrinsic CO shift rate of *R. gelatinosus* CBS2, including the dependence on ambient CO concentration.

Bioreactor Development For Biological H <sub>2</sub> Production NREL						
Task Designation/Milestone	FY2002					2003
	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4	Qtr 1
<b>Task 1: Investigate Pressurized Bioshift Reactors</b>						
Operate bioreactor at a system pressure of 10 atm					★	
<b>Task 2: Measuring the Intrinsic CO Shift Rate of <i>Rubrivivax gelatinosus</i> CBS2</b>						
Measure the specific CO shift rate of <i>R. gelatinosus</i> CBS2					◆	

FY2002 Begins October 1, 2001      ★ = Critical Milestone      ◆ = Milestone

## **Biomass-Derived Hydrogen from a Thermally Ballasted Gasifier – Iowa State University of Science and Technology**

The goal of this project is to optimize performance of an indirectly heated gasification system that converts switch grass into hydrogen-rich gas suitable for powering fuel cells. Iowa State University has developed a thermally ballasted gasifier that uses a single reactor for both combustion and pyrolysis. Instead of spatially separating these processes, they are temporally isolated. The producer gas is neither diluted with nitrogen or the products of combustion. The heat released during combustion at 850°C is stored as latent heat in the form of molten salt sealed in tubes immersed in the fluidized bed. During the Pyrolysis phase, which occurs at temperatures between 600 and 850°C, the reactor is fluidized with steam rather than air. Heat stored in the phase change material is released during this phase of the cycle to support the endothermic reactions of the pyrolysis stage.

Because air is not used during the gas-producing phase of the cycle, nitrogen does not dilute the product gas, resulting in relatively high concentrations of hydrogen and carbon monoxide in the producer gas compared to conventional gasifiers. In preliminary trials Iowa State has measured hydrogen content between 20 and 36 vol-%, which is a factor of 4 to 6 higher than found in gas from air-blown gasifiers. The thermal ballasting system also more than doubles the carbon monoxide concentration. The carbon monoxide, along with steam used to fluidize the reactor, can be shifted to additional hydrogen by the water-gas shift reaction.

The approach to this project is to amply a pilot-scale (5 ton per day) gasifier to evaluate the thermally ballasted gasifier as a means for producing hydrogen from switchgrass. Gasification at the pilot scale is important for obtaining realistic process data, especially for calculating energy flows through the system and assessing the practicality of feeding switch grass into the gasifier. A series of gasification trials will be preformed to evaluate the effect of biomass feed rate (fixed steam rate) and the effect of biomass/steam rate (fixed biomass feed rate) on hydrogen production.

A slipstream from the gasifier will be used to evaluate gas cleaning and upgrading options during the first year of research. This slipstream will include: a guard bed designed to remove hydrogen sulfide and hydrogen chloride and some tar; a steam reformer designed to crack the remaining tar and decompose ammonia; and high temperature and low temperature catalytic hydrogen content. A series of gasification trials will be performed to evaluate the effectiveness of these four reactors in removing tar and contaminants, and shifting producer gas towards increased hydrogen and decreased carbon monoxide.

### **Task 1: Prepare Switchgrass Fuel and Feeder**

Switchgrass will be delivered as square bales from the Chariton Valley Biomass Power project in southern Iowa. The bales will be dismantled by hand and fed into a hammer mill. Different screens used in conjunction with the hammer mill will achieve desired particle sizes. A 0.5 inch screen will normally result in a maximum top size of 1 inch, which is acceptable for the 5 tonne/day gasification system. The fuel system consists of charge hopper, bucket elevator, rotary airlock, and metering hopper. The metering hopper, consisting of a screw auger with a variable frequency drive to control rotational speed, is used to control the fed rate of material. The equipment is in place and is fully operational.

### **Task 2: Prepare Gasifier**

A 5-ton/day bubbling fluidized bed gasifier and a latent heat ballasting system are already available for this research. The gasifier will be modified to operate as a ballasted gasifier. This entails installation of the ballast system within the bed of the gasifier as well as adding additional plumbing for gas and steam flows to the reactor. Mixtures of nitrogen and steam will be used to fluidize the reactor during the pyrolysis stage of the gasification cycle. A steam system will be installed, which will include a boiler,

heat exchange, superheater, and associated piping. A nitrogen delivery systems with associated plumbing will be installed as well. Load cells will be installed on the flue metering system to accurately measure fuel flow into the gasification reactor. Thin-film heat flux sensors, thermocouples, and hot wire anemometers will be added to improve energy and mass balance calculations on the system.

### **Task 3: Prepare Slipstream for Upgrading Producer Gas**

Upgrading producer gas from the biomass gasifier consists of four steps. After particulate removal, the producer gas passes through a high temperature guard bed to remove hydrogen sulfide and hydrogen chloride. Trace contaminant removal is followed by steam reforming to convert tar into low molecular weight compounds, convert methane into hydrogen and carbon monoxide, and decompose ammonia. Third and fourth steps consist of high and low temperature water-gas shift reactions, respectively, to increase hydrogen content of the gas and remove carbon monoxide. The pilot-scale gasifier operating with the ballast system produces as much as 200 m<sup>3</sup>/hr of producer gas. During the first year, Iowa State University plans to work with a slipstream of only 4 m<sup>3</sup>/hr of the gasifier output to study producer gas cleaning and upgrading.

### **Task 4: Prepare Gas Sampling and Analysis System**

Gas-sampling trains will be assembled to measure raw gas composition as well as monitor changes in gas composition before and after the various catalytic reactors. One gas sampling train will draw samples directly from the gasifier exhaust pipe. This isokinetic sampling system is designed to accurately measure concentrations of particulate matter, tar, and trace contaminants as well as quantify the major constituents of the producer gas. A series of valves will allow two of the sampling trains to simultaneously analyze gas from the inlet and outlet of any one of the four reactors.

### **Task 5: Perform Gasification Trials**

The following trials will be performed: 1) Effect of biomass feed rate, 2) Evaluate the effect of biomass/steam ratio by substituting nitrogen to fluidize the bed, 3) Baseline test for energy and mass balance evaluation, 4) Baseline test for contaminant levels, 5) Evaluate guard bed, 6) Evaluate steam reforming reactor, 7) Evaluate water-gas shift reactors, 8) Collaborative exchange of data with University of Victoria, BC, Canada.

### **Task 6: Economic Evaluation**

Capital investment, operating costs, and production costs for hydrogen will be estimated using standard engineering estimation methods that we have used in previous studies of fuels derived from biomass

### **Task 7: Annual Report**



**Biomass-Derived Hydrogen from a Thermally Ballasted Gasifier  
Iowa State University of Science and Technology**

Task Designation/Milestone	FY2002					2003
	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4	Qtr 1
<b>Task 1: Prepare Switchgrass Fuel and Feeder</b>						
Baled switchgrass from Chariton Valley		◆				
Debaled and chop switchgrass as needed					◆	
Configure feeder system		◆				
<b>Task 2: Prepare Gasifier</b>						
Install strain gages and heat sensors		◆				
Fabricate and install ballast system		◆				
<b>Task 3: Prepare Slip Stream</b>						
Install guard bed			◆			
Install steam reformer			◆			
Install water-gas shift reactors			◆			
<b>Task 4: Prepare Gas Sampling System</b>						
Particulate sampling			◆			
Tar				◆		
Gaseous species				◆		
<b>Task 5: Gasification Trials</b>						
Effect of gasifier operating conditions				★		
Performance of downstream reactors					◆	
<b>Task 6: Economic Evaluation</b>						
Capital costs					◆	
Operating costs					◆	
<b>Task 7: Final Report</b>					◆	

FY2002 Begins October 1, 2001



★ = Critical Milestone



◆ = Milestone

## SEPARATION AND PURIFICATION

### Separation Membrane Development – Westinghouse Savannah River Technology Center

The goal of this project is to develop an energy efficient hydrogen separation process based on a new class of composite materials. This new separation process will resist harmful impurities in the feed stream such as oxygen and carbon monoxide, and will be energy efficient. The approach that will be investigated is an absorption process using sol-gel encapsulated metal hydride material. It is known that metal hydrides absorb hydrogen reversibly and can be used to separate hydrogen from other gases. The problem with metal hydrides is that they can be poisoned by impurities such as oxygen and carbon monoxide, and that they break up to small particles too fine for use in separation columns. Earlier work at the Savannah River Technology Center has showed that using a sol-gel process, metal hydride particles can be encapsulated in a highly porous silica matrix. The porosity can be controlled so that the pores permit hydrogen to reach the metal hydride but prevent the larger molecule impurities such as oxygen and carbon monoxide from poisoning the reactivity of the metal hydride. The silica matrix also serves as a granular substrate for the small metal hydride particles so that packing a column is not a problem. These results indicate that hydrogen separation columns can be produced using the encapsulated metal hydride particles. The column will absorb hydrogen from a gas mixture when it is cooled and will release the absorbed hydrogen when it is heated to produce a high purity hydrogen stream.

The goal of this project is commensurate with the overall goals of the DOE Hydrogen R&D Program to make hydrogen competitive with other energy sources. Cost-effective and efficient hydrogen separation is needed both in the short-term, to facilitate the successful transition of hydrogen from fossil-based sources as well as the long-term, to develop hydrogen from renewable sources, like biomass.

The largest volume of hydrogen produced today (> 90%) is produced at the point of use by petroleum refineries and ammonia manufacturers. Discussion with major US companies in both of these two industries indicates significant interest in SRTC hydrogen separation and recovery technology. Applications of SRTC sol-gel, metal hydride technology to smaller stationary and onboard partial oxidation (POX) systems as well as to the recovery of hydrogen from biomass derived fuels are also being investigated.

#### **Task 1: Conduct Separation Test in Laboratory Scale**

This hydrogen separation concept involves the use of a packed column. The packing material will be the sol-gel encapsulated metal hydride. Both the temperature and the hydrogen pressure will be cycled, so that hydrogen in a gas mixture is absorbed during the low temperature or the high pressure half-cycle. A laboratory scale column will be used for the testing. The following subtasks are identified:

- 1a: Conduct separation tests on hydrogen mixtures with nitrogen
- 1b: Conduct separation tests on hydrogen mixtures with moisture, methane and carbon monoxide
- 1c: Repeat test with improved sol-gel encapsulated metal hydrides

#### **Task 2: Develop Low Cost Sol-gel Metal Hydride System**

The cost of metal hydride needs to be reduced to make this process economically favorable. Effort will be made to work with a commercial metal hydride manufacturer to develop a low cost material for this system. The subtasks are:

- 2a: Identify a commercial hydride manufacture to develop a low cost metal hydride
- 2b: Conduct parametric study of sol-gel encapsulation with a low cost metal hydride

**Task 3: Conduct Cost Analysis to Compare This System to Present Technology**

The sol-gel encapsulated metal hydride absorbs hydrogen but not the other components in the mixture. It can be used in a temperature swing or pressure swing process. Present technology uses zeolite in a pressure swing absorption process to purify hydrogen. The zeolite adsorbs non-hydrogen components in the mixture. The cost of these two systems will be compared.

<b>Separation Membrane Development</b> <b>Westinghouse Savannah River Technology Center</b>						
Task Designation/Milestone		FY2002				2003
	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4	Qtr 1
<b>Task 1: Conduct hydrogen separation tests</b>						
1a: Conduct separation tests on H <sub>2</sub> /N <sub>2</sub>		◆				
1b: Tests on H <sub>2</sub> /H <sub>2</sub> O, H <sub>2</sub> /CH <sub>4</sub> , H <sub>2</sub> /CO				★		
1c: Repeat tests with improved sample						◆
<b>Task 2: Develop low cost sol-gel MH system</b>						
2a: Identify metal hydride manufacturer			◆			
2b: Parametric study with low cost MH					◆	
<b>Task 3: Conduct cost analysis</b>					◆	

FY2002 Begins October 1, 2001      ★ = Critical Milestone      ◆ = Milestone

## **Defect-free Thin Film Membranes for H<sub>2</sub> Separation and Isolation – Sandia National Laboratories**

This project, begun in December 1999, is focused on the research and development of crystalline, inorganic, molecular sieve (zeolite) thin film membranes for light gas molecule separations. In particular, we are interested in separating and isolating H<sub>2</sub> from CH<sub>4</sub>, CO, CO<sub>2</sub> and N<sub>2</sub> gases. Current hydrogen separation membranes are based on Pd alloys or on chemically and mechanically unstable organic polymer membranes. The use of molecular sieves brings a stable (chemically and mechanically stable) inorganic matrix to the membrane. The crystalline frameworks have “tunable” pores that are capable of size exclusion separations. Sandia envisions impact of positive results from this program in the near term with Hydrocarbon fuels, and long term with Biomass fuels.

During this reporting period, Sandia focused their research on (1) the synthesis of defect-free selective zeolite membranes, and (2) the synthesis of microporous phosphate-based phases for applications in light gas molecular sieving. To date, they have synthesized high flux, selective membranes that separate H<sub>2</sub> from N<sub>2</sub>, CH<sub>4</sub> and CO<sub>2</sub>. The phases grown are known aluminosilicate zeolite phases. The permeation and selectivity values are unprecedented, even though the films have been grown on both sides of the support. Also, Sandia has exciting new discussions with Pall Corporation for possible future collaborations; Pall Corporation is a leader in porous membrane support manufacturing. Test stainless steel membrane supports have been provided to Sandia for initial testing. Furthermore, they have synthesized new microporous phases with pore sizes in the range for light gas separations.

### **Project Tasks for FY2002:**

Plans for next year include the continuation of Sandia’s work on synthesis, modeling and thin film growth of novel microporous phases for light gas separations, including novel gallo phosphates and silicotitanate phases. Furthermore, they plan to explore the thin film growth of aluminosilicates zeolites doped with other elements for maximized adsorption and selectivity of H<sub>2</sub> over other light gases of interest.

Sandia will also continue to build interactions and collaborations with outside industries for potential future collaborations and commercialization partnerships. In particular, they are focusing on suppliers of industrially valuable stainless steel based supports.

### **Task 1: Thin Film and Bulk Growth**

Subtask 1.1: Growth of aluminosilicate (Al/Si) zeolite thin films on disk supports (single sided).

Subtask 1.2: Growth of aluminosilicate (Al/Si) zeolite thin films on tube supports (internal; industrially valuable).

Subtask 1.3: Growth of aluminosilicate (Al/Si) and metal doped films with various pore cations (ion exchange or as-synthesized).

Subtask 1.4: Synthesis of defect-free gallophosphate (Ga/P) and silicotitanate (Si/Ti) phases as thin film membranes (with 100% coverage, <50µm thick).

Subtask 1.5: Synthesis of bulk phosphate and titanate novel phases

Subtask 1.6: Characterization of all new phases (X-ray diffraction, thermal analyses, surface area, and elemental analysis).

### **Task 2: Permeation Studies**

Subtask 2.1: Permeation studies of pure gases through membranes, RT and 80°C.

Subtask 2.2: Amend permeation unit to study mixed gases (Mass Spec or Residual Gas Analyzer augmentation)

Subtask 2.3: Permeation studies of mixture gases through membranes, RT and 80°C.

### Task 3: Modeling and Simulation

Subtask 3.1: Model separation values by molecular dynamics calculations for **pure** light gases interacting with the novel Al/Si and Si/Ti frameworks.

Subtask 3.2: Model separation values by molecular dynamics calculations for **mixtures of** light gases interacting with the novel Al/Si and Si/Ti frameworks.

### Task 4: Business Development

Subtask 4.1: Initiate procedures for eventual industrial collaboration

Subtask 4.2: Investigate follow-on funding possibilities for industrial partnerships

Defect-free Thin Film Membranes for H <sub>2</sub> Separation and Isolation Sandia National Laboratories						
Task Designation/Milestone	FY2002					2003
	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4	Qtr 1
<b>Task 1: Thin Film and Bulk Growth</b>						
Growth of Al/Si thin films, disk supports			◆			
Growth of Al/Si thin films, tube supports						★
Growth of Al/Si thin films, various cations					◆	
Synthesis of defect-free Ga/P and Si/Ti				◆		
Synthesis of bulk Ga/P and Si/Ti		◆				
Characterization of all new phases					◆	
<b>Task 2: Permeation Studies</b>						
Pure gases, RT and 80°C				◆		
Amend Permeation unit			◆			
Mixed gases, RT and 80°C					★	
<b>Task 3: Modeling and Simulation</b>						
Molecular dynamics calc., <b>pure</b> light gases (Al/Si, Si/Ti)			◆			
Molecular dynamics calc., <b>mixed</b> light gases (Al/Si, Si/Ti)					◆	
<b>Task 4: Business Development</b>						
Initiate procedures				★		
Investigate follow-on funding possibilities					◆	

FY2002 Begins October 1, 2001      ★ = Critical Milestone      ◆ = Milestone

Table 3.2 Renewable Production		
Goal: Advance emission-free, and renewable-based hydrogen production technologies towards commercial viability, with a target cost of \$10-\$15/MMBtu.		
Category	Project	Researchers
<i>Electrolytic Processes</i>	Solar Photocatalytic H <sub>2</sub> Production from Water using a Dual Bed Photosystem	Florida Solar Energy Center
	Photoelectrochemical Based Direct Conversion for Hydrogen Production	National Renewable Energy Laboratory
	Photoelectrochemical Hydrogen Production	University of Hawaii
	Combinatorial Discovery of Photocatalysts for Hydrogen Production	SRI International
	Photoelectrochemical Hydrogen Production using New Combinatorial Chemistry Derived Materials	University of California, Santa Barbara
<i>Photobiological Processes</i>	Maximizing Photosynthetic Efficiencies and Hydrogen Production by Microalgal Cultures	University of California, Berkeley
	Molecular Engineering of Algal Hydrogen Production	National Renewable Energy Laboratory
	A Cyclic Photobiological Algal Hydrogen Production System	National Renewable Energy Laboratory
	International Energy Agency and Other International Collaborations	National Renewable Energy Laboratory
	Efficient Hydrogen Production Using Enzymes of the Pentose Phosphate Cycle	Oak Ridge National Laboratory

## ELECTROLYTIC PROCESSES

### Solar Photocatalytic H<sub>2</sub> Production from Water Using a Dual Bed Photosystem – Florida Solar Energy Center

Photocatalytic compounds in particulate form will be employed in various dual modular configurations so as to effect the solar-driven decomposition of water to its constituent elements, particularly hydrogen. The system advantages are low manufacturing cost, safe evolution of H<sub>2</sub> and O<sub>2</sub> in separate compartments, and more efficient use of the solar spectrum.

Each module has its own distinctive photocatalyst according to whether it is to evolve H<sub>2</sub> or O<sub>2</sub>. Earlier studies concentrated on conventional inorganic semiconductor materials. It was eventually realized that new photocatalytic materials needed to be developed to avoid lifetime problems due to corrosion and to absorb lower energy photons. A combination of semi-empirical molecular orbital calculations and voltammetric, UV-visible spectroscopic, and UV photoelectron analysis identified several organic pigment families as promising materials. The perylenes gave the best results for O<sub>2</sub> evolution, while the phthalocyanines proved best for H<sub>2</sub> evolution. Even so, these “best” results were only in the 10-100 microliter range for 2.8 cm<sup>2</sup> substrates under irradiation from a UV-filtered Xe lamp for six hours. The quantum efficiencies are quite low, even though the molar extinction coefficients for these materials are exceptionally high. More effort into the photodecay processes that limit the necessary water-splitting chemistry are in order.

The tasks to be performed over the next year are as follows:

#### **Task 1: Investigation of controlling factors in solar conversion efficiency**

Florida Solar Energy Centre's (FSEC) system calculations based on materials costs indicate that if an 8% solar to hydrogen conversion efficiency could be obtained, the resulting H<sub>2</sub> would sell for \$13/mbtu. To achieve this efficiency, it is anticipated that a combination of photocatalyst materials and system configuration development will be necessary. For this year the emphasis will be on determining the fate of absorbed solar photons by the photocatalysts, i.e., what is the quantum efficiency for charge transfer in FSEC's system and how it can be improved.

Thin films of pigment photocatalysts will be fabricated via spraying and vacuum evaporation and then examined for the following effects:

- a. **co-catalyst effect:** the application of small amounts of catalytic metals and metal oxides to the organic light-absorbing material has proved vital to the performance of the photoparticles, and so will be monitored as to activity versus loading and deposition conditions.
- b. **molecular doping:** the addition of molecular agents to the pigments that act as dopants and promote higher photoconductivity will be further studied.
- c. **thermal annealing:** heat treating to improve crystallinity and ultimately photoconductivity will be attempted.
- d. **film thickness:** the trade-off between better light absorption as organic films become thicker and conductivity improvements as they become thinner will be studied and optimized.

**Task 2: Continued photocatalyst development**

- a. **O<sub>2</sub>-evolving photocatalyst.** For O<sub>2</sub> evolution, derivatization of the imide moiety on the perylene diimide is expected to improve its photocatalytic performance.
- b. **H<sub>2</sub>-evolving photocatalyst.** Depending on the experimental results, various quinacridones, indanthrones, and phthalocyanines will be employed, depending on which is most compatible with optimum operating conditions

**Task 3: Module construction**

Successful completion of tasks 1 and 2 will lead to construction and testing of photocatalytic modules.

- a. **Photocatalyst and co-catalyst distribution.** The means of applying a 1.0 weight percent co-catalyst uniformly distributed over a large photocatalyst deposit area is a technique that must be developed. Chemical reduction, electrochemical deposition, and simple physical blending of co-catalysts have been attempted in the past. The task here is to develop a combination of photocatalyst, co-catalyst, and reducing agent that are compatible with each other.
- b. **Testing under solar illumination.** This will be the critical milestone, to construct dual modules and test them under solar illumination. FSEC also has a solar simulator that can produce up to 1.5 AM1 solar irradiance over an area of many square meters. Other groups at the Center have used it for testing solar hot water heaters, photovoltaic cells, and calibrating of optical test equipment. If necessary FSEC can secure beam time on the simulator and construct a module of whatever area is necessary to obtain a measurable gas evolution rate.

**Task 4: Participation in IEA Annex activities**

FSEC will participate in Annex 14 on "Photoelectrolytic Production of Hydrogen." FSEC's work should fit in well with the overall collaboration on dye-sensitized photoelectrochemical systems.



**Solar Photocatalytic H<sub>2</sub> Production from Water Using a Dual Bed Photosystem  
Florida Solar Energy Center**

Task Designation/Milestone	FY2002					2003
	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4	Qtr 1
<b>Task 1: Investigation of controlling factors in solar efficiency</b>						
a. co-catalyst effect	◆					
b. molecular doping		◆				
c. thermal annealing			◆			
d. ffilm thickness					◆	
<b>Task 2: Continued photocatalyst development</b>						
a. O <sub>2</sub> -evolving photocatalyst		◆				
b. H <sub>2</sub> -evolving photocatlyst			◆			
<b>Task 3: Module construction</b>						
a. photocatlyst and co-catalyst distribution					◆	
b. testing under solar simulator					★	
<b>Task 4: Participation in IEA Annex 14 activities</b>						
a. attend fall '01 experts meeting	◆					
b. attend spring '02 experts meeting			◆			

FY2002 Begins October 1, 2001

★ = Critical Milestone

◆ = Milestone

## **Photoelectrochemical Based Direct Conversion for Hydrogen Production – National Renewable Energy Laboratory**

The goal of this research is to develop a stable, cost effective, photoelectrochemical based system that splits water upon illumination, producing hydrogen and oxygen directly, using sunlight as the only energy input. Practical high efficiency systems could achieve 18-24% efficiency, low cost multi-junction amorphous silicon systems could achieve 7-12% efficiency.

A photoelectrochemical (PEC) system combines the harvesting of solar energy with the electrolysis of water. When a semiconductor of the proper characteristics is immersed in an aqueous electrolyte and irradiated with sunlight, the energy can be sufficient to split water into hydrogen and oxygen. Depending on the type of semiconductor material and the solar intensity, this current density is 10-30 mA/cm<sup>2</sup>. At these current densities, the voltage required for electrolysis is much lower, and therefore, the corresponding electrolysis efficiency is much higher. At a current density similar to short-circuit photocurrent from an ideal PEC water splitting system, hydrogen and oxygen generation is achieved at an effective applied voltage of approximately 1.35 V, giving rise to an electrolysis efficiency of 91% [LHV]. *Note that 1.35 volts is less than the thermodynamic potential required to split water. The additional energy needed for the reaction comes from the surrounding environment as heat. If one were to run a continuous electrolysis at 1.35 volts in an insulated environment, the solution would cool down and eventually freeze. However, for this solar energy application, heat is available from the sunlight as infrared photons that are not being used by the semiconductor, so a continuous electrolysis at 1.35 volts is possible. If one were to use the higher heating value for hydrogen of 1.48 volts, a PEC system operating at an equivalent voltage of 1.35 would have an electrolysis efficiency of 110%, again, this is only possible because of the availability of additional solar energy in the form of heat.* One of the major advantages then of a direct conversion photoelectrochemical system is that it not only eliminates most of the costs of the electrolyzer, but it also has the possibility of increasing the overall efficiency of the process leading to a further decrease in costs.

For direct photoelectrochemical decomposition of water to occur, several key criteria of the semiconductor must be met. The semiconductor band gap must be sufficient to split water (~1.7eV), the semiconductor band edges must span both the redox potentials of the hydrogen and oxygen evolution reactions, and finally the charge transfer from the surface of the semiconductor must be fast enough to not only prevent corrosion but also reduce or eliminate band edge migration. Gallium indium phosphide (GaInP<sub>2</sub>), the semiconductor used in this research, has a band gap of 1.8 - 1.9eV, thus meeting the first of the criteria. Its band edges, however, do not overlap that of water. The electrode also accumulates charge at its surface, thus contributing to surface corrosion and leading to band edge migration away from the desired band edge potentials. NREL has been successful in catalyzing the surface of GaInP<sub>2</sub>, and they have also been successful in moving the band edges sufficiently positive that a direct water splitting system using only GaInP<sub>2</sub> might be possible. This is a landmark accomplishment, because it represents the first time that a semiconductor band edges have been moved from a position where they energetically could not do a reaction, to a potential where a reaction is possible. The fact that this may allow water splitting makes this accomplishment even more significant. This ability to control the band edges also has implications for NREL's PV/PEC tandem cells, in that control of the band edges would allow them to maximize the efficiency of the tandem cell system.

As well as determining proper surface treatments for enhancement of reaction rates, and stabilizing the surface, NREL is also working at identifying new semiconductors with suitable properties for PEC water splitting, and designing and optimizing multijunction cell technology for photoelectrolysis systems.

Photoelectrochemical systems have long been recognized as having the capability of producing highly efficient photon conversion devices at relatively low cost, and NREL's work has shown that water splitting via photoelectrochemistry is technical feasible.

### **Task 1: Bandedge Engineering for Increased Water Splitting Efficiency**

Before a semiconductor can produce hydrogen and oxygen, the conduction band and the Fermi level of the semiconductor must extend beyond the water redox potentials. This is a problem with GaInP<sub>2</sub>, in that the conduction band and Fermi level do not overlap the water redox potentials. Additionally, under illumination, electrons build up on the semiconductor surface, shifting the bandedges and Fermi level further away from overlap of the water redox potentials. NREL has been working on surface treatments with metallated porphyrins and transition metals to suppress bandedge migration and engineer the bandedges so that overlap can occur. Their results indicate that coating the GaInP<sub>2</sub> surface with ruthenium octaethylporphyrin carbonyl (RuOEP CO) can shift the bandedges up to 600 mV, allowing the bandedges to overlap the water redox potentials. Additionally, coating the GaInP<sub>2</sub> surface with RuCl<sub>3</sub> catalyzed charge transfer from the semiconductor to the water, reducing bandedge migration under light irradiation. Future work will focus on the long-term surface stability of these new treatments and quantitative applications of porphyrins. NREL will work to determine if indeed, the engineered, catalyzed, GaInP<sub>2</sub> surface will accomplish water splitting. This milestone is a very ambitious milestone, but would create a great deal of interest should we be successful.

### **Task 2: Characterization of New Materials and Tandem Cells**

NREL has achieved direct water electrolysis with a novel integrated monolithic photoelectrochemical-photovoltaic design. This photoelectrochemical cell, voltage biased with an integrated photovoltaic device, splits water directly upon illumination; light is the only energy input. The hydrogen production efficiency for this system based on the short-circuit current and the lower heating value of hydrogen is 12.4%. Because of its high efficiency, efforts will continue to identify, and understand the factors that limit the efficiency and lifetime of this system. Continuing research will also study the corrosion mechanisms and possible passivating techniques. Further experiments are planned to look at surface pretreatments (from Task 1) to see if NREL can increase the overall efficiency and the lifetime of the catalytic coat.

As part of NREL's search for semiconductor materials with inherently greater stability, they have initiated a study of nitride materials. It is known that GaN is chemically very stable, so much so that device fabricators have not been able to develop a suitable wet chemical etchant for it. It is also known that the composition of In<sub>x</sub>Ga<sub>1-x</sub>N can be adjusted to produce a band gap suitable for solar applications. The NREL PV group is also working on these materials, but not the specific compositions the researchers for this project are interested in. They will be looking for industrial partners to grow samples tailored to their specific requirements.

### **Task 3: Low Cost Amorphous Silicon Multijunctions**

NREL has been testing a variety of a-Si triple-junction and a-SiC samples that they have obtained from Energy Conversion Devices. Current-voltage tests looking at corrosion showed that a-SiC protects the a-Si triple-junction material in electrolyte solution, but decreases the current density as compared to the non-protected a-Si of the same design. Mott-Schottky measurements showed that NREL's a-SiC samples had a .75 Ω-1 Ω resistance under illumination. They believe that this resistance could explain the decrease in the current density. Also, different metal-ion solutions were applied to the semiconductors by drop-evaporation methods. Tests showed that some of these metal-ion solutions do increase current density. Two standard a-Si triple-junction devices displayed almost no corrosion as well as the highest current density. Further work will be done on these samples with the metal-ion solutions as surface catalysts.

For this work NREL is partnering with Energy Conversion Devices to grow samples specifically for water splitting.

**Task 4: System design**

NREL will continue to develop designs for working PEC water splitting systems that can be studied by the Process Analysis group. The best multijunction design/catalytic system will be determined and NREL will study both high efficiency and low cost systems.

<b>Photoelectrochemical Based Direct Conversion Systems for Hydrogen Production</b> <b>National Renewable Energy Laboratory</b>						
Task Designation/Milestone		FY2002				2003
	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4	Qtr 1
<b>Task 1: Bandedge Engineering for Increased Water Splitting Efficiency</b>						
2% water splitting efficiency for surface modified single layer p-GaInP <sub>2</sub>					◆	
<b>Task 2: Characterization of New Materials and Tandem Cells</b>						
Characterization of available materials for stability and water splitting activity				◆		
<b>Task 3: Low Cost Amorphous Silicon Multijunctions</b>						
4% water splitting efficiency for a triple junction a-Si structure					★	
<b>Task 4: System design</b>						
Provide data to system designers as required					◆	
FY2002 Begins October 1, 2001      ★ = Critical Milestone      ◆ = Milestone						

## **Photoelectrochemical Hydrogen Production – University of Hawaii, Manoa**

High efficiency photoelectrochemical systems to produce hydrogen directly from water using solar energy as the power source is one of the technologies identified to meet the Department of Energy's mission for renewable hydrogen production. In order to meet DOE goals, such a system must be low cost, must operate at solar to chemical conversion efficiencies greater than 10% and must have long operating lifetimes. Photoelectrochemical research at the University of Hawaii (UH) has focused on the development of integrated multijunction photoelectrodes, comprising semiconductor, catalytic and protective thin films deposited on low-cost substrates for producing hydrogen using direct solar energy. Integrated electrical/optical/electrochemical models have been used to develop multijunction amorphous silicon (a-Si) photoelectrodes with expected solar-to-hydrogen conversion efficiencies up to 10%, and copper-indium-gallium-diselenide (CIGS) photoelectrodes with expected conversion efficiencies up to 15%.

As an alternative approach to the integrated a-Si and CIGS photoelectrode structures, UH recently developed the conceptual design for a hybrid solid-state/PEC photoelectrode incorporating current-matched solid-state and electrochemical photojunctions. This design was motivated both by recent advances in semiconductor materials for photoelectrochemical applications, such as dye-sensitized  $\text{TiO}_2$ ,  $\text{WO}_3$ , and  $\text{Fe}_2\text{O}_3$ , and by modeling experiences in multijunction solid-state cell design. Important advantages of the advanced hybrid design include elimination of lateral current collection, reduction in the front surface overpotential, and simplification of device lateral geometry for ease of fabrication. In addition, there could be greater long-term stability based on the thick, seamless outer layer (of  $\text{TiO}_2$ ,  $\text{WO}_3$ , or  $\text{Fe}_2\text{O}_3$ ) in this structure.

Based on an evaluation of the relative advantages and disadvantages of the integrated a-Si, the integrated CIGS, and the hybrid photoelectrode configurations under consideration, we have formulated a plan of attack for FY 2002 work. The plan stresses development of the hybrid configuration, and also emphasizes demonstration of the side-by-side configured CIGS multijunction photoelectrode structure. The research approach focuses on continued use of integrated models for photoelectrode design; establishment of industry partners with materials expertise and fabrication capabilities, and fabrication and testing of photoelectrode test structures. Specific task activities include:

### **Task 1: Triple-Junction a-Si Integrated Electrodes**

The integrated triple-junction stacked a-Si structure reported in previous years has been important as a proof-of-concept for integrated photoelectrode operations. However, based on the predicted solar-to-hydrogen efficiencies limited to 10%, we do not plan to further develop photoelectrodes in this configuration. UH does plan to complete testing of a-Si devices in further efficiency and stability experiments. Information obtained from evaluation of these multijunction solid-state photoelectrodes will be invaluable in the development of the hybrid design, which incorporates a double- or triple-junction a-Si cell.

### **Task 2: Triple-Junction CIGS Integrated Photoelectrodes**

Based on the predicted solar-to-hydrogen efficiencies in excess of 10%, UH plans continued development and optimization of the side-by-side CIGS design. Although proof-of-concept CIGS photoelectrodes fabricated to date at HNEI have been based on the mechanically interconnected scheme, this configuration is impractical from a commercial standpoint. Fabrication of the side-by-side junctions using commercial planar processing techniques is essential to the successful development of a CIGS photoelectrode. An important part of our effort will be the identification of potential industry partners for producing side-by-side CIGS test structures for incorporation into the photoelectrode configuration for evaluation. By the end of the research period, we plan to have completed a plan for fabricating

demonstration photoelectrodes using the industry-supplied CIGS cells with catalyst and encapsulation post-processing performed at UH. UH also plans to upgrade our in-house CIGS deposition system to produce sample films and diodes for efficiency and corrosion studies.

### **Task 3: Hybrid a-Si Solid-State/PEC Photoelectrodes**

As an important third activity, UH plans to initiate research to develop the hybrid solid-state/PEC device structure, specifically configured using a double- or triple-junction a-Si photocell with an appropriate current-matched PEC outer junction to be determined as part of the research. Initial stages of this work will require literature surveys of promising semiconductor coatings for the PEC junction, such as dye-sensitized  $\text{TiO}_2$ ,  $\text{WO}_3$ , and  $\text{Fe}_2\text{O}_3$ . UH also plans to establish partnerships with research organizations specifically developing these materials for photoelectrochemical applications to take advantage of their expertise and experience. The optical, photoelectrochemical, and corrosion data obtained for the dye-sensitized  $\text{TiO}_2$ ,  $\text{WO}_3$ , and  $\text{Fe}_2\text{O}_3$  semiconductor materials in various electrolyte environments will be used in the selection of the most promising PEC junctions for this application. Using the obtained material performance data, UH plans to adapt our integrated model to formulate initial designs for a prototype hybrid solid-state/PEC photoelectrode. By the end of this research period, they plan to have completed fabrication and initial testing of the prototype.

Consistent with the “Future Plans” presented in the Annual Review in April 2001, the important task milestones can be summarized as follows:

#### Task Activity 1

- Complete testing of triple-junction a-Si photoelectrodes in process
- **KEY:** Complete evaluation of stability and efficiency issues and prepare publications

#### Task Activity 2

- Adapt integrated model to CIGS photoelectrode configuration to optimize efficiency
- Identify potential industry partners to produce side-by-side CIGS test structures
- Upgrade in-house CIGS deposition capabilities
- **KEY:** Develop plan to fabricate and test integrated CIGS multijunction photoelectrodes

#### Task Activity 3

- Establish partnerships with research organizations developing  $\text{TiO}_2$ ,  $\text{WO}_3$ , and  $\text{Fe}_2\text{O}_3$
- Adapt integrated model to hybrid system to optimize efficiency
- Determine most promising hybrid system based on available information
- **CRITICAL:** Fabricate and test prototype hybrid device

**Photoelectrochemical Hydrogen Production**  
**University of Hawaii, Manoa**

Task Designation/Milestone		FY2002					2003
		Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4	Qtr 1
<b>Task 1. a-Si Triple Junction Photoelectrodes</b>							
(a) Complete testing of photoelectrodes in process			◆				
(b) Complete evaluation of stability and efficiency for publication				◆			
<b>Task 2. CIGS Integrated Photoelectrodes</b>							
(a) Adapt integrated model to CIGS photoelectrode configuration				◆			
(b) Identify industry partners to fabricate side-by-side CIGS				◆			
(c) Upgrade in-house CIGS fabrication facility					◆		
(d) Develop plan to fabricate and test CIGS photoelectrodes					◆		
<b>Task 3. Hybrid Photoelectrodes</b>							
(a) Establish partnerships with research organizations developing TiO <sub>2</sub> , WO <sub>3</sub> , and Fe <sub>2</sub> O <sub>3</sub>			◆				
(b) Adapt integrated models to hybrid systems				◆			
(c) Determine appropriate hybrid system for initial fabrication					◆		
(d) Fabricate and test prototype hybrid photoelectrode							★

FY2002 Begins October 1, 2001



= Critical Milestone



= Milestone

## **Combinatorial Discovery of Photocatalysts for Hydrogen Production – SRI International**

The goal of this effort is the production of hydrogen via the photolytic splitting of water. In Phase 1, which will begin in September of 2001, SRI will develop a combinatorial approach to identify semiconductor substrates, surface modification(s), and experimental conditions that lead to the efficient splitting of water to produce hydrogen. Their specific objective in Phase 1 of the proposed effort is to develop and validate a combinatorial workstation that can be used to screen an array of materials in terms of electrochemical properties and photocatalysis.

### **Task 1: Combinatorial Cell Development**

This task describes the apparatus configuration for evaluating electrochemical and photochemical properties. The focus of the first year will be to build the prototype apparatus and test it on selected materials. In following years it will be used to provide a database of semiconductor materials and catalysts for use in rapid discovery of new materials capable of efficiently producing hydrogen from water.

For the first phase of the project, FY 2002, SRI proposes to build a simple prototype system with individually addressable and compartmentalized cells. Once the prototype system is optimized and validated to provide the requisite accuracy and performance, they will increase the capacity of the system and provide additional automation. The optimization and validation process will be conducted with well-characterized materials.

### **Task 2: Sample Preparation**

In this task, semiconductor systems suitable for water splitting will be prepared. The proposed samples to be evaluated in Phase 1 of this effort will include nanophase powders produced by our partner and commercially available substrates. The powders will include semiconductor powders such as  $\text{TiO}_2$  and doped  $\text{TiO}_2$  materials produced in various sizes, phases and dopant levels using a proprietary synthetic process.

### **Task 3: Hydrogen Production Screening**

To test for water splitting activity SRI plans to subject the materials to illumination under a xenon light source. The samples will be illuminated from the bottom using a light table and will be subjected to irradiation for a selected period of time. The array will have septum tops, which will be loaded in an inert atmosphere so that no oxygen will be in the vials before illumination. The gases formed will be analyzed using a head space analyzer for determination of hydrogen and oxygen production. Actinometry measurements will be conducted to ensure that the intensity of the light source is uniform in all positions.

### **Task 4: Database Generation and Interpretation**

In this task, SRI will collect data on the band gap, flat band potential, hydrogen and oxygen efficiency as a function of semiconductor type, modifications, electrocatalysts, and other conditions. In Year 2, SRI plans to incorporate the data into a program such as Spotfire, which will allow them to rapidly visualize the data and help find new materials and electrocatalysts.



**Combinatorial Discovery of Photocatalysts for Hydrogen Production**  
**SRI International**

Task Designation/Milestone	FY2002					2003
	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4	Qtr 1
<b>Task 1. Combinatorial Cell Development</b>						
(a) Prototype Design		◆				
(b) Test Single cell for functionality and optimize			◆			
(c) Build multi-cell prototype			◆			
(d) Validate multi-cell prototype				★		
<b>Task 2. Sample preparation</b>						
(a) Develop combinatorial strategy		◆				
(b) Obtain/synthesize materials			◆			
(c) Material characterization				◆		
<b>Task 3. Hydrogen production</b>						
(a) Reactor set-up			◆			
(b) Test reactor and optimize				◆		
(c) Implement automate sampling and data acquisition					★	
<b>Task 4. Database generation and interpretation</b>						
(a) Generate database					◆	
(b) Develop models						◆

FY2002 Begins October 1, 2001



= Critical Milestone



= Milestone

## **Photoelectrochemical Hydrogen Production Using New Combinatorial Chemistry Derived Materials – University of California**

The overall project objective is the development and application of combinatorial methods to discover an efficient, practical, and economically sustainable system for photoelectrochemical production of bulk hydrogen from water. University of California, Santa Barbara (UCSB) will attempt to accomplish this by introducing a shift in the research paradigm from the present method of conventional serial chemical research to a combinatorial approach featuring a systematic and deliberate high-speed exploration of the composition-structure-property relationship of new metal-oxide based solid-state materials. By intelligent and rapid design, synthesis, and analysis of large diverse collections of potential catalytic and photoelectrochemical systems (called “libraries”), UCSB, will attempt to discover new and useful energy-producing materials as well as better understand fundamental mechanism and composition-structure-function relationships of these materials.

**Task 1:** Design and Construct a Versatile Automated System and Develop the Methodologies for Automated Electrochemical Synthesis of Combinatorial Libraries of Mixed Metal Oxides

**Task 2:** Define Electrosynthetic Routes Amenable to the Automated Synthesis System for Doped Mixed Metal Oxides which can be Synthesized by a Combination of Electrochemical Deposition.

**Task 3:** Develop an Automated High-throughput Photoelectrochemical Screening System for Measuring I-V, Photocurrent, Flatband Potentials, Bandgap, and Electrochemical Potential of Combinatorially Prepared Photocatalyst Libraries.

**Task 4:** Create and Screen Libraries of Materials, which Include Well Known Oxides to Validate the Methodology by Comparing Observed Performance Trends to Known Behavior

**Task 5:** Complete the Development of a Chemo-optical Detection System Based on Optical Sensing of the Reduction of Tungsten Oxide as a High-throughput Screening System for Monitoring

**Task 6:** Begin Exploratory Synthesis and Screening of New Metal-oxide Systems and Begin to Examine Composition-structure-function relationships and the relationship between screened properties (photocurrent, bandgap, flat-band potential) and catalytic performance in hydrogen photocatalysis

**Task 7:** Design and Synthesize Libraries of Potential Patterned Metal Oxides Using Diverse Types of Structure Directing Agents (e.g. Anionic and Non-ionic Surfactants, and Block Copolymers) Under a Variety of Deposition Conditions to Explore Synthesis Structure Relationships for Nanostructured Metal/Metal Oxide Thin Films with Accessible Pores and High Surface Areas

**Task 8:** Specify Database Requirements for a Large-scale Combinatorial Discover Project and Begin Establishing Appropriate Data Structures

**Task 9:** Synthesize and Screen in Year 1 at Least Three Libraries and Perform Detailed Conventional Analytical Studies to Validate the Electrochemical Synthesis Methodology

## PHOTOBIOLOGICAL PROCESSES

### Maximizing Photosynthetic Efficiencies and Hydrogen Production in Microalgal Cultures – University of California, Berkeley

The goal of the research is to generate green algal strains with enhanced photosynthetic productivity and hydrogen production under mass culture conditions. To achieve this goal, it is first necessary to optimize the optical and light-utilization properties of the cells. This requirement entails a reduction in the number of the chlorophyll (Chl) molecules that service the two photosystems and will translate into significantly greater solar conversion efficiencies of microalgae in mass culture. Thus, efforts are under way to isolate microalgal mutants with a truncated chlorophyll antenna size.

Immediate objective of the research is to identify genes that confer a truncated Chl antenna size in the model green alga *Chlamydomonas reinhardtii*. Identification of such genes in *Chlamydomonas* will permit a subsequent transfer of this property, i.e., “truncated Chl antenna size”, to other microalgae of interest to the DOE Hydrogen Program.

This objective is currently being approached through physiological manipulations, DNA insertional mutagenesis/screening and biochemical/molecular analyses of *Chlamydomonas reinhardtii* cells. A truncated light-harvesting Chl antenna size for photosystem-II and photosystem-I has been identified in three different mutants and some of the genes that confer this property are at hand.

#### **Rationale and Significance**

The rationale and justification of this research is that a truncated light-harvesting Chl antenna size in green algae will minimize the ability of individual cells to absorb sunlight. In consequence, photosynthesis in individual cells would not become saturated, even under bright sunlight, and absorbed solar energy would not be wasted by thermal dissipation. Thus, in mass culture of high cell density, a truncated Chl antenna size will permit an overall greater solar energy conversion efficiency and productivity as it will minimize (i) wasteful dissipation of absorbed sunlight, and (ii) mutual cell shading. A feasibility study was conducted on the question of maximizing solar use efficiency and productivity in green algae by minimizing the Chl antenna size of the photosystems. It was shown that, in mass culture, algal strains which possessed a truncated Chl antenna size could exhibit ~3 times greater rates of photosynthesis and hydrogen production than could be achieved with fully pigmented cells. Thus, the research seeks to develop *Chlamydomonas* strains having a permanently truncated Chl antenna size, and to isolate and characterize the genes and proteins that regulate the Chl antenna size of photosynthesis. This information will find direct application in photobiological hydrogen production.

#### **Task Statement**

The research will continue along the lines of recent progress in order to clarify the regulation and function of specific genes shown to control the Chl antenna size of photosynthesis in green algae. Further, working with the green alga *Chlamydomonas reinhardtii*, the research will pursue identification of additional genes that confer a truncated Chl antenna size. The following subtasks are envisioned:

##### **A. DNA analysis of the *tla1* insertional transformant**

Complete the DNA sequencing of the *ARG7* insertion site in the *tla1* *Chlamydomonas* transformant. Initiate a study of expression patterns of the *tla1* gene under different irradiance conditions. Assess the functional role of the interrupted *tla1* ORF.

**B. Initiate *tlal* mutant complementation studies**

Upon completion of the *tlal* gene cloning in the wild type, initiate efforts to test for the ability of the wild type gene to complement the “truncated Chl antenna” phenotype in the *tlal* mutant. Such transformation of the mutant, and recovery of the wild type phenotype, will provide a simple but direct and essential test that the whole gene, responsible for the truncated Chl antenna phenotype, has been isolated.

**C. Investigate mechanism of *CAO* (chlorophyll *a* oxygenase) gene expression**

Initiate efforts to elucidate the signal transduction pathway for the regulation of *CAO* gene expression by irradiance in order to better understand how *CAO* gene expression affects the Chl antenna size in green algae.

**D. DNA insertional mutagenesis library**

Initiate efforts to expand the DNA insertional mutagenesis library (from 6,500 to ~15,000 transformants) in order to identify additional “Chl antenna size” mutants. Screen new transformants by the Chl *a/b* ratio measurement rather than by fluorescence imaging analysis. Barriers: Time consuming nature of the Chl *a/b* ratio screen.

**E. Solar conversion efficiency and H<sub>2</sub> production measurements in wild type and *tlal* mutants**

Initiate measurements on solar conversion efficiency and hydrogen production in selected *Chlamydomonas reinhardtii* wild type and transformants with a truncated Chl antenna size.

**F. Preparation of reports on the results and publication of the work in peer-reviewed journals.**

Maximizing Photosynthetic Efficiencies and Hydrogen Production in Microalgal Cultures University of California, Berkeley						
Task Designation/Milestone		FY2002				2003
	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4	Qtr 1
A. DNA analysis of the <i>tlal</i> insertional transformant			◆			
B. Initiat <i>tlal</i> mutant complementation studies				◆		
C. Investigate mechanism of <i>CAO</i> (Chl <i>a</i> oxygenase) gene espression		◆				
D. DNA insertional mutagenesis library					◆	
E. Solar conversion efficiency and H <sub>2</sub> production measurements in wild type and <i>tlal</i> mutants				★		
F. Preparation of reports and publication in peer-reviewed journals					◆	

FY2002 Begins October 1, 2001      ★ = Critical Milestone      ◆ = Milestone

## **Molecular Engineering of Algal Hydrogen Production – National Renewable Energy Laboratory**

The goal of this project is to generate O<sub>2</sub>-tolerant, H<sub>2</sub>-producing mutants from the green alga *Chlamydomonas reinhardtii*, test them in a laboratory-scale system for continuous photoproduction of H<sub>2</sub> under aerobic conditions and collaborate with other national laboratories and universities in improving the efficiency of algal H<sub>2</sub> production.

The project objectives for FY 2002:

- Successfully generate mutated hydrogenase genes and start to re-introduce them into wild-type *C. reinhardtii* cells.
- Conduct expression studies of HydB, the second hydrogenase to determine its function.

Hydrogen production by green algae has significant advantages over other photobiological systems: ATP production is not required, high theoretical efficiencies are possible, and water is used directly as the source of reductant without the need to store intermediary carbon metabolites. Currently, the main practical biological limitations to using green algae for photobiological H<sub>2</sub>-production are the sensitivity of the reversible hydrogenase (the enzyme that release H<sub>2</sub> gas) to O<sub>2</sub> and low algal photosynthetic conversion efficiencies at solar light intensities. NREL is addressing the former problem, by generating and selecting for O<sub>2</sub>-tolerant, H<sub>2</sub>-producing mutants of *C. reinhardtii* using molecular genetic approaches.

There is sufficient precedent in the literature to warrant attempts to generate an O<sub>2</sub>-tolerant hydrogenase by molecular genetic means in *C. reinhardtii* at this time. For example, O<sub>2</sub>-tolerant hydrogenases have been reported in non-photosynthetic bacteria, photosynthetic bacteria, and *C. reinhardtii* mutants (although mutants in the latter organism were not preserved for future studies). Also, studies involving site-directed mutagenesis of the uptake hydrogenase from the bacterium *Azotobacter vinelandii* indicate that a single amino acid change in the sequence of one of the subunits of the enzyme improves the O<sub>2</sub>-tolerance of the enzyme. Previous results funded under last year's project include the isolation of two generations of mutants, using classical mutagenesis techniques, that have shown up to a factor of 10 increase in O<sub>2</sub> tolerance.

NREL has cloned two putative Fe-only hydrogenase genes (HydA and HydB) in *C. reinhardtii*. The HydA gene cloned in our lab is 100% homologous to a *C. reinhardtii* hydrogenase gene cloned by L. Mets last year, contains the 24 amino acid residues present in the N-terminal portion of the isolated *C. reinhardtii* reversible hydrogenase, and shows a high degree of homology to previously cloned Fe hydrogenases from anaerobic bacteria. The HydB gene has a similar degree of homology to other Fe hydrogenases, and contains all the motifs characteristics of those enzymes. However, since its corresponding protein has not been isolated, NREL will need to get physiological and biochemical evidence that it encodes for another hydrogenase, and to study the conditions under which it is expressed.

This year, NREL will apply mutagenesis techniques, start to re-introduce mutated genes in wild-type *C. reinhardtii* cells, and select for mutants with improved O<sub>2</sub> tolerance. They will also examine possible functional aspects associated with the HydB gene. The generation of hydrogenase mutants will be achieved by error-prone PCR, a technique that utilizes variations in the polymerase chain reaction (PCR) conditions to allow the introduction of random errors during the replication of a specific DNA sequence. The mutated genes will then be re-introduced into wild-type *C. reinhardtii* by electroporation, and the resulting strains will be chemochromically screened for O<sub>2</sub>-tolerance.

**Task 1: Complete research on the cloning of the two algal hydrogenase genes**

Final experiments are being performed, including expression studies (Northern and Western blots, and activity induction experiments) and studies to determine the number of genes encoding for HydA and HydB (Southern blots).

**Task 2: Mutagenize the isolated hydrogenase genes**

NREL will develop an error-prone PCR mutagenesis technique with the isolated HydA gene, initially, in order to generate genes containing random mutations. The technique will have to be optimized for *C. reinhardtii*. Optimization of the technique will involve testing different primer:substrate ratios and determining the percentage of mutations per amplification reaction. In order to accomplish this task, representative clones from each reaction will have to be sent out for sequencing and subsequent analysis at NREL.

**Task 3: Investigate the physiological role of HydB in algal H<sub>2</sub> production**

HydA has been identified as the gene that codes for the reversible hydrogenase (by its homology to the protein isolated by Happe in 1993), but the function of HydB is currently not known. Three approaches will be considered to address this problem: (a) physiological studies relating the level of H<sub>2</sub> production with the relative amount of transcript (mRNA) for HydB; (b) construction of an oligopeptide based on the amino acid sequence of HydB, deduced from the gene nucleotide sequence, conjugation of this oligopeptide to a rabbit protein and generation of specific antibodies against it; and (c) overexpression of the HydB gene in *E. coli*, purification of the protein, and generation of specific antibodies against it. The availability of antibodies by either (b) or (c) will then allow us to study the expression of the HydB protein in *C. reinhardtii* cells under different environmental conditions.

**Molecular Engineering of Algal H<sub>2</sub> Production  
NREL**

Task Designation/Milestone	FY2002					2003
	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4	Qtr 1
<b>Task 1: Complete research on the cloning of the two algal hydrogenase genes</b>						
Complete the cloning work			◆			
<b>Task 2: Mutagenize the isolated hydrogenase genes</b>						
Develop techniques to perform error-prone PCR on the HydA reversible hydrogenase gene			◆			
<b>Task 3: Investigate the physiological role of HydB in algal H<sub>2</sub> production</b>						
Complete physiological studies of HydB expression					★	

FY2002 Begins October 1, 2001

★ = Critical Milestone

◆ = Milestone

## **A Cyclic Photobiological Algal Hydrogen Production System – National Renewable Energy Laboratory**

The goal of this project is to understand and improve a cyclic system for H<sub>2</sub> photoproduction based on partial, reversible inactivation of photosynthetic O<sub>2</sub> evolution in *Chlamydomonas reinhardtii* by depriving the cells of sulfate.

Project Objectives for FY 2002 are to

- Investigate parameters (pH, high light treatment and temperature shock) that may accelerate the inactivation of O<sub>2</sub> evolution in sulfur-depleted *C. reinhardtii*.
- Complete the construction of a new photobioreactor system.

Last year NREL showed that re-addition of sulfate to sulfur-depleted cells at the beginning of the sulfur-deprivation period enhances residual photosynthetic O<sub>2</sub> evolution activity and specific rates of H<sub>2</sub> production, particularly if light/dark synchronized cultures are used. In order to further pursue these results, and to study the effect of O<sub>2</sub> re-addition to the cultures, it will be necessary to build a more controllable photobioreactor system that is able to sense redox potential in the cultures and respond to it by injecting more O<sub>2</sub> and/or sulfate into the reactor. Dr. Anatoly Tsygankov from Pushchino, Russia, will be collaborating with us in addressing these engineering issues.

**Task 1:** Study the effects of pH, high light and/or high temperature on the inactivation of photosynthetic O<sub>2</sub> evolution by sulfur-depleted algal cultures.

The inactivation of photosynthetic O<sub>2</sub> evolution by sulfur depletion, a *sine qua non* for subsequent algal H<sub>2</sub> production, currently takes 24 h on the average. The literature has examples of other procedures that also reversibly inactivate O<sub>2</sub> evolution, such as low pH, temperature shock and photoinhibition, among others. It is possible that the combination of some of these methods with sulfur depletion will lead to a faster start of the H<sub>2</sub> production phase. Preliminary experiments indicate that either high light or low pH treatment does indeed accelerate inactivation of PSII activity, but these treatments may also affect the total yield of H<sub>2</sub>. The combination of low pH with high light and high temperature, followed by sulfur depletion, may result in substantially faster PSII inactivation and earlier start of H<sub>2</sub> production.

**Task 2:** Study the effect of the addition of controlled amounts of O<sub>2</sub> on H<sub>2</sub> production rates, with the purpose of circumventing low redox potential regulation of photosynthetic electron transport. Experiments will be done using the new photobioreactor.

Recent biochemical evidence strongly indicates that the reductants necessary for photobiological H<sub>2</sub> production by sulfur-depleted algal cells originate mainly from the residual photosynthetic activity of these cells. Furthermore, some H<sub>2</sub> production may also result from substantial internal protein degradation. Current rates of H<sub>2</sub> production are about 25% of the maximum rates, predicted as a result of measured residual photosynthetic H<sub>2</sub>O oxidation by Photosystem II (PSII), suggesting that only one fourth of the electrons generated from H<sub>2</sub>O are being utilized for H<sub>2</sub> production. It is clear that steady-state H<sub>2</sub> production is limited by factors other than the number of active PSII centers. Understanding the source of this limitation at the physiological and molecular level may allow us to circumvent it and take advantage of the full potential of photosynthetic electron transport by the cultures. The literature indicates that the low redox potential prevalent during the H<sub>2</sub> production phase may down-regulate photosynthetic electron transport. The redox potential could be raised by introducing small and controlled amounts of O<sub>2</sub> to the cultures. Introduction of too much O<sub>2</sub>, on the other hand, would inactivate the hydrogenase, and thus decrease the rates of H<sub>2</sub> production. However, a balance between the amount of added O<sub>2</sub> and the redox potential may result in higher electron transport and hydrogenase activity.



**Cyclic Photobiological Algal H<sub>2</sub>-Production  
National Renewable Energy Laboratory**

Task Designation/Milestone	FY2002					2003
	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4	Qtr 1
<b>Task 1: Study the effects of pH, high light and/or high temperature on the inactivation of photosynthetic O<sub>2</sub> evolution by sulfur-depleted algal cultures</b>						
Complete study of low pH inactivation			◆			
<b>Task 2: Study the effect of the addition of controlled amounts of O<sub>2</sub> on H<sub>2</sub> production rates, with the purpose of circumventing low redox potential regulation of photosynthetic electron transport. Experiments will be done using the new photobioreactor</b>						
Complete studies of O <sub>2</sub> addition					★	

FY2002 Begins October 1, 2001

★ = Critical Milestone

◆ = Milestone

## **International Energy Agency and Other International Collaborations – National Renewable Energy Laboratory**

The objective of this project is to foster international collaborations and technology transfer for the advancement of hydrogen production, storage and utilization technologies. Included is support for activities conducted within the framework of the International Energy Agency (IEA). NREL provides the Secretariat function as well as the Task Leader for the Integrated System activities and experts for the Photoelectrochemical Hydrogen Production, Carbon for Hydrogen Storage, Hydrogen Production from Carbon Containing Materials and Integrated Systems tasks, all for the IEA Hydrogen Agreement and provides an expert on biomass pyrolysis and pyrolysis oils for the IEA Bioenergy Agreement and an expert in solar thermal production of hydrogen to the IEA SolarPACES Agreement. This project also provides support for an international collaboration to develop steam reforming of bio-oil with the University Rovira i Virgili, Spain.

### **Task 1: Secretariat support**

NREL is responsible for the day-to-day operations of the IEA Agreement on the Production and Utilization of Hydrogen and serves as the administrative arm of the Executive Committee. This includes organizing and reporting on the Executive Committee meetings, producing the Annual Report, managing the Common Fund, monitoring the progress of all Annex activities, and reporting to IEA Headquarters, as well as coordinating various strategic planning activities.

### **Task 2: Integrated Systems operations (IEA Hydrogen Agreement Annex 13)**

The objective of Annex 13, Design and Optimization of Integrated Systems, is to develop a tool to assist in the design and evaluation of potential hydrogen demonstration projects and in the optimization of existing hydrogen demonstration projects. Emphasis is placed on integrated systems covering all components, from input energy to end-use. The activities are focused on near- and middle- term applications, with consideration of the transition to sustainable hydrogen energy systems. Life cycle assessments are performed on comparative hydrogen systems.

NREL serves as the Operating Agent (OA) for Annex 13. In this capacity, overall organization and technical and administrative management of the activity are required. In addition, the OA is required to report on a regular basis to the Executive Committee, and to provide detailed reports as stipulated in the Annex 13 work plan.

Annex 13 will complete its work in June 2002. Presentations on the results of the activity will be made at the 14<sup>th</sup> World Hydrogen Energy Conference, as well as published in final IEA Task Reports. In addition to completing the Annex 13 work, emphasis will be placed on developing a new IEA Task to continue the integrated systems work. This will include organizing a task development workshop and preparing a draft program of work.

### **Task 3: International collaborations**

**Participation in IEA Hydrogen Agreement Integrated Systems Activities:** Existing and proposed hydrogen energy system demonstrations typically deploy technologies at different levels of development. A combination of data collection, demonstration case studies, component simulation, integrated systems modeling and life cycle assessment will result in the development of design guidelines for future demonstrations.

NREL expertise in life cycle analysis and process simulation and analysis are critical to the success of this activity. Participation is required in Subtask A (Model Development) and Subtask B (Systems Analysis) of Annex 13.

The results from the Life Cycle Analyses completed during FY2001 will be compiled into a final report. The model development will be completed and reported in an IEA technical report.

**Participation in IEA Collaborative on the Study of the Amorphous Silicon Carbide/Electrolyte Interface and other Novel Water Splitting Systems (Hydrogen Agreement Annex 14, Photoelectrolytic Production of Hydrogen):** The aim of this task is to develop a stable semiconductor/electrolyte based water splitting system. This is a joint effort involving researchers from the University of Geneva and the University of Berne in Switzerland, Uppsala University in Sweden, and the National Renewable Energy Laboratory. This cooperative research program uses the strength and capabilities of each member of the research team.

This research involves the growing and characterization of various compositions and structures of thin films. NREL is conducting solid state and material characterization including SIMS, XPS and Auger, and studying the semiconductor/electrolyte interface using impedance spectroscopy. The University of Geneva is studying the fundamental photoelectrochemical properties, including photocurrent voltage measurements and spectral response. The goal of this research is to determine the best composition and growth parameters that give rise to the most stable interface while maintaining high conductivity and optical transparency, as well as studying some new structures for possible application as water splitting devices.

With the University of Geneva, Switzerland, NREL will be investigating some novel configurations involving a unique tungsten trioxide ( $\text{WO}_3$ ) electrode that they have developed. These electrodes will only split water with a 0.6 V external bias. NREL proposes to provide this bias with an amorphous silicon tandem cell from ECD. The configuration would be a standard  $\text{WO}_3$  electrode on glass with an a-Si cell directly behind it. This could be a very inexpensive water splitting setup, since NREL could use the standard commercial a-Si cells, and they would never be in contact with the electrolyte. Also the  $\text{WO}_3$  is infinitely stable in water. As part of this collaboration, Ms. Clara Santos from the University of Geneva visited NREL for two months in the summer of 1999 to perform some experiments. NREL determined the band edge positions for a few  $\text{WO}_3$  samples. As expected, the material is n-type, but there is some variability in the measured band edge position. This is important as it determines the nature of the a-Si cell NREL uses to make the tandem device. Ms. Santos is finishing her PhD, and is applying for a Swiss scholarship for a postdoctoral position at NREL. NREL will continue this work should she receive this scholarship.

Uppsala University (Sweden) has developed synthetic procedures for "purpose built materials;" that is, the controlled assembly of  $\text{Fe}_2\text{O}_3$ ,  $\text{ZnO}$  and Ru oxides in the nanoparticle regime into various shapes. Moreover, these samples can be prepared on flexible substrates. NREL's initial investigations of this new  $\text{Fe}_2\text{O}_3$  material showed that it has higher quantum yields than the regular material, but has a low efficiency due to the thin film not absorbing much light. Stability is also an issue. NREL is continuing to evaluate this material for water splitting. This will involve some changes in the synthesis, and some adjustments in the experimental procedures.

A new project has been initiated with Professor Gion Calzaferri at the University of Berne, Switzerland. He has a catalytic system that uses a silver-based photo-electrode to produce oxygen under illumination. Since  $\text{GaInP}_2$  will produce hydrogen (but not oxygen), NREL has given him some  $\text{GaInP}_2$  electrodes to try in his system to see if a tandem configuration will be able to split water.

Two projects are in the discussion stages with countries that are considering joining the Annex (and the IEA Hydrogen Agreement). One of the projects involves Australia (and possibly New Zealand), and

would be aimed at developing an integrated amorphous silicon system for water splitting. The second project involves Mexico and would focus on thin film systems based on copper-gallium-indium diselenide systems. Dr. Arturo Fernandez from UNAM, Mexico is spending his sabbatical year at NREL, and is working with NREL to develop a joint collaborative project during that time.

**Photobiological Production of Hydrogen:** Biological hydrogen production, the production of  $H_2$  by microorganisms, has been an active field of basic and applied research for over two decades, with significant applied R&D programs supported in Europe, Japan and the USA. The IEA Hydrogen Agreement has had active tasks focusing on this subject for six years now, starting with the recently completed Annex 10, Photoproduction of Hydrogen, and now with the new Annex 15, Photobiological Production of Hydrogen. The recent advances in producing measurable quantities of hydrogen using green algae are of significant importance to the success of this international collaboration. NREL's significant expertise in this area will be essential to the success of this task.

This year NREL researchers will collaborate with international representatives from the University of Uppsala, Sweden, the Norwegian Institute for Water Research, the University of Montreal, Canada, and the University of California to further the fundamental understanding of the genetics, biochemistry and physiology of hydrogenase functions, including the metabolism and factors affecting growth of microalgae.

**Participation in IEA Pyrolysis Activity:** The IEA Bioenergy Pyrolysis Task was approved for another three-year term, taking it through December 2003. Compared to the previous term activities, the Task will be more focused on implementation and market opportunities. The objectives are to review the field of fast pyrolysis of biomass in order to identify both technical and non-technical barriers to faster and wider spread of the technology and, thus, to contribute to improving the rate of its implementation. At this time, the Task includes 16 member countries: Austria, Belgium, Denmark, Finland, France, Germany, Greece, Ireland, Italy, Netherlands, Norway, Portugal, Spain, Sweden, UK, and US. A few other countries have also expressed interest in the activity. The IEA Task 34 is integrated with the EC Pyrolysis Network PyNe, which, together with the European gasification group GasNet, form a cluster called ThermoNet. The Task is comprised of five Topic Groups: Applications; Environment, Health, and Safety; Norms, Standards, and Characterization; Charcoal Production; and Technical and Non-technical Barriers. Additionally, two topics of common interest to PyNe and GasNet will be carried out jointly: Pyrolysis Vapor Treatment and Education/Training. PyNe will also participate in two projects approved by the EC Altener program. One project will carry out a study on the competitiveness of bio-oil in a variety of heat and power applications in all of the European countries. The other project will investigate norms and standards for bio-oil. NREL will lead the Applications Group, as well as provide input into all of the other activities.

**Collaboration with the University Rovira i Virgili (Spain):** For the past five years, this collaborative effort has resulted in significant advances in the area of steam reforming bio-oil and hemicellulose-rich liquids from biomass fractionation processes to produce hydrogen. The focus has been on other biomass-derived liquids (vegetable oils and byproducts from bio-diesel processes) as feedstocks for the steam reforming process. This effort has been carried out through a researcher exchange program between NREL and the University Rovira i Virgili with funding support from the Commission for Cultural, Educational and Scientific Exchange. NREL will continue to work with the group in Spain to identify funding sources for the collaboration and to further the technology.

**Collaboration for the Development of Carbon Nanotubes for Hydrogen Storage:** IEA Task 17 began work in June 2001 and will continue through May 2004. In support of this continuing collaboration for hydrogen storage, NREL is working with Prof. Richard Chahine at l'Universite du Quebec a Trois-Rivieres. This activity is focused on obtaining adsorption isotherms on raw and purified single-wall carbon nanotube materials with different kinds of probe molecules ( $He$ ,  $Ar$ ,  $CH_4$ ,  $H_2$ , etc). The purified materials are supplied in either annealed or unannealed forms that are expected to have different internal

surface area properties. Initially, supplied materials are not activated for hydrogen storage. These background experiments will yield information that will be relevant to understanding these materials for hydrogen storage applications. Activated samples will be subsequently supplied.

**Support for the Project Development of a New IEA Activity on Hydrogen Production for Carbon Containing Materials:** This new IEA Task is expected to be approved to begin work in October 2001 and will consist of three Subtasks: Large-Scale Production, Biomass to Hydrogen and Small-Scale Reformers. NREL has extensive expertise in the area of biomass conversion and utilization and will lead the Subtask on Biomass to Hydrogen. The Subtask will be a joint effort with the IEA Bioenergy Gasification and Pyrolysis activities.

During FY2001, the state-of-the-art report on biomass to hydrogen technologies will be published as an IEA technical report. Commitment letters from the participating countries will be finalized. A kick-off meeting will be planned and held during Spring 2002 to finalize the work plan and formally launch the activity.

<b>International Energy Agency and Other International Collaborations National Renewable Energy Laboratory</b>						
Task Designation/Milestone	FY2002					2003
	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4	Qtr 1
<b>Task 1: Secretariat support</b>						
Fall 2001 Executive Committee Meeting		◆				
Spring 2002 Executive Committee Meeting				◆		
2001 Annual Report					◆	
<b>Task 2: Integrated Systems operations (IEA Hydrogen Agreement Annex 13)</b>						
Draft Program of Work					★	
<b>Task 3: International collaborations</b>						
State-of-the-Art Report – Biomass to Hydrogen		◆				
Final Experts Meeting/Task Development Workshop				◆		
FY2002 Begins October 1, 2001      ★ = Critical Milestone      ◆ = Milestone						

The following table summarizes international travel planned for FY2002. In addition, several people are planning to attend the 14<sup>th</sup> World Hydrogen Energy Conference (WHEC), scheduled for June 2002 in Montreal, Canada. The WHEC is considered by most people in the Hydrogen Community to be the definitive platform for technology transfer of all international hydrogen research, development, demonstration, deployment, analysis, and outreach information. The DOE Hydrogen Program supports WHEC financially through its Broad-based Solicitation. The WHEC participants are listed following the table.

### International Travel

Traveler	Place	Date	Reason for Travel
<b>DOE Headquarters</b>			
Neil Rossmeissl	Budapest, Hungary	December 01	IEA Executive Committee Meeting
Neil Rossmeissl	Lithuania	May 02	IEA Executive Committee Meeting
<b>National Renewable Energy Laboratory</b>			
Cathy Grégoire Padró	Budapest, Hungary	December 01	IEA Executive Committee Meeting
Cathy Grégoire Padró	Lithuania	May 02	IEA Executive Committee Meeting
Cathy Grégoire Padró	Tokyo, Japan	November 01	Hydrogen Forum
Carolyn Elam	Budapest, Hungary	December 01	IEA Executive Committee Meeting; Executive Secretary (Time Only)
Carolyn Elam	Lithuania	May 02	IEA Executive Committee Meeting; Executive Secretary (Time Only)
Jim Ohi	Paris	October 01	ISO/TC 197 Meeting, Hydrogen Joint Working Group (HJWG) meeting
Jim Ohi	Tokyo, Japan	November 01	Hydrogen Forum, HJWG meeting
Bob Evans	Norway	April 02	IEA Annex 16 Meeting
Al Lewandowski	Europe	June 02	SolarPACES Experts Meeting
Stefan Czernik	Austria	January 02	IEA Pyrolysis Activity meeting
Stefan Czernik	TBD-Europe	August 02	IEA Pyrolysis Activity meeting
1 person TBD	Netherlands	April 02	World Congress on BioHydrogen Technologies
1 person TBD	Netherlands	April 02	World Congress on BioHydrogen Technologies
John Turner	Japan	August 02	IEA Annex 14 Experts Meeting
Mike Seibert	Europe	March 02	IEA Annex 15 Experts Meeting
1 person TBD	Netherlands	April 02	World Congress on BioHydrogen Technologies
Mike Seibert	Japan	September 02	IEA Annex 15 Experts Meeting
<b>Sandia National Laboratories</b>			
Karl Gross	Annecy, France	September 02	International Symposium on Metal Hydrogen Systems (MH2002); Invited (Time Only)
Eric Majzoub	Annecy, France	September 02	MH2002
Gary Sandrock	Budapest, Hungary	December 01	IEA Hydrogen Executive Committee Meeting
Gary Sandrock	Lithuania	May 02	IEA Hydrogen Executive Committee Meeting
Gary Sandrock	TBD	TBD	IEA Task 17 Experts' Workshop
Principal Investigator TBD	TBD	TBD	IEA Task 17 Meeting

**WHEC Participants****DOE Headquarters***Two of the following:*

Neil Rossmeissl

Sigmund Gronich

Christopher Bordeaux

**National Renewable Energy Laboratory***Four of the following:*

Cathy Grégoire Padró

Carolyn Elam

Jim Ohi

Michael Heben

Pamela Spath

Roland Pitts

Robert Evans

Stefan Czernik

**Savannah River Technology Center***Two of the following:*

Theodore Motyka

William Summers

Leung Heung

Ragaiy Zidan

## **Efficient Hydrogen Production Using Enzymes of the Pentose Phosphate Cycle – Oak Ridge National Laboratory**

Although in theory the amount of hydrogen that could be generated from renewable sources of energy such as cellulose (a polymer of glucose) is vast<sup>1</sup>, only 16-24% of the maximum stoichiometric yield of hydrogen from glucose (about 12 mol H<sub>2</sub> per mol glucose) is typically achieved by biological methods<sup>2</sup>. Here we show that the enzymes of the oxidative pentose phosphate cycle<sup>3-5</sup> can be coupled to hydrogenase purified from the Archaeon *Pyrococcus furiosus*, one of only a few hydrogenases that use NADP<sup>+</sup> as the electron carrier<sup>6</sup>, to generate 11.6 mol H<sub>2</sub> per mol glucose-6-phosphate. Hydrogen produced by this pathway is the major product, unlike that produced by intermediate metabolic pathways of bacterial fermentation, and therefore has important practical implications for biohydrogen production<sup>7</sup>.

The oxidative branch of the pentose phosphate cycle containing glucose-6-phosphate (G6P) dehydrogenase and 6-phosphogluconate (6PG) dehydrogenase converts G6P to ribulose-5-phosphate (Ru5P), with the formation of 2 mol NADPH and 1 mol CO<sub>2</sub>. Incubation of G6P and NADP<sup>+</sup> with these dehydrogenases and the *P. furiosus* hydrogenase generates the maximum possible stoichiometric yield of H<sub>2</sub>, 2 mol per mol G6P<sup>8</sup>. However, when all the enzymes of the oxidative pentose phosphate cycle apart from 6-phosphogluconolactonase were mixed with the hyperthermophilic hydrogenase, NADP<sup>+</sup> and G6P, 11.6 mol H<sub>2</sub> per mol G6P were generated<sup>8</sup>.

### **Overall Task:**

Production of H<sub>2</sub> from renewable sugar at close to theoretical yields using recombinant forms of hyperthermophilic hydrogenase and enzymes of the pentose phosphate pathway. If this could be achieved practically this would represent a major innovation that would advance our abilities to develop an efficient and practical system for bio-hydrogen production.

### **Task Activities for FY 2002:**

**Task 1:** Glucose-6-phosphate dehydrogenase (G6PDH) and 6-phosphogluconate dehydrogenase (6PGDH) homogeneously purified and fully characterized. Optimize the expression and purification of recombinant thermophilic oxidative Pentose Phosphate enzymes

**Task 2:** Full comparison of rates and yields of H<sub>2</sub> production by thermophilic and mesophilic enzymes (G6PDH and 6PGDH).

**Task 3:** Purification and characterization of the native wild-type enzymes from *T. maritima* Comparison of properties of the wild-type and recombinant forms of these enzymes, e.g. in terms of stability, k<sub>cat</sub>, K<sub>m</sub>, V<sub>max</sub>. This work will result in new knowledge showing the advantage of using thermophilic enzymes for the generation of molecular hydrogen from renewable energy.



Efficient Hydrogen Production Using Enzymes of the Pentose Phosphate Cycle UT-Battelle, LLC						
Task Designation/Milestone		FY2002				2003
	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4	Qtr 1
Expression of both thermophilic pentose phosphate enzymes	★					
Homogeneous purification of pentose phosphate enzymes		◆				
Kinetic & Thermal Characterization of both enzymes		◆				
Incorporation of enzymes into H <sub>2</sub> /CO <sub>2</sub> production process		◆				
Purification & characterization of wild-type enzymes from <i>Thermotogamaritima</i>				◆		
Isolation of other thermophilic PP enzymes from <i>Thermotogamaritima</i>					◆	

FY2002 Begins October 1, 2001      ★ = Critical Milestone      ◆ = Milestone

### 3.1.2 Hydrogen Storage Research Projects

A key component of hydrogen R&D is the development of storage systems for hydrogen. Stationary storage systems are needed to provide hydrogen for electricity generation to complement distributed and intermittent renewable resources and to store off-peak energy for use during peak energy periods. Stationary storage systems will also be needed at vehicle refueling stations. Safe, lightweight hydrogen storage systems are needed for storing hydrogen on-board vehicles. Program hydrogen storage R&D is being conducted using carbon structures as well as metal hydride systems. Storage tasks are summarized in Table 3.3.

<b>Table 3.3</b> <b>Hydrogen Storage Research</b>		
<b>Goal: Demonstrate safe and cost-effective storage systems for use in stationary distributed electricity generation applications, and for on-board and stationary applications in non-attainment areas.</b>		
<b>Category</b>	<b>Project</b>	<b>Researchers</b>
<i>Carbon Structures</i>	Carbon Nanotube Materials for Hydrogen Storage	National Renewable Energy Laboratory
	Doped Carbon Nanotubes for Hydrogen Storage	Westinghouse Savannah River Technology Center
	Hydrogen Storage in Metal-Modified Single-Walled Carbon Nanotubes	California Institute of Technology
<i>Metal Hydrides</i>	Catalytically Enhanced Hydrogen Storage Systems	University of Hawaii
	Hydrogen Storage Development	Sandia National Laboratories
	Hydrogen Storage in Alanes	United Technologies Research Center
	Complex Hydrides for Hydrogen Storage	Florida Solar Energy Center
<i>Physical Storage</i>	Vehicular Hydrogen Storage Using Lightweight Tanks	Lawrence Livermore National Laboratory and Idaho National Energy Engineering Laboratory
	Advanced Thermal Hydrogen Compression	Ergenics, Inc.

## CARBON STRUCTURES

### **Carbon Nanotube Materials for Hydrogen Storage – National Renewable Energy Laboratory**

The goals of this project are to understand the interactions which stabilize hydrogen on single-wall carbon nanotubes, to controllably access the sites which strongly and reversibly bind hydrogen, to produce large quantities of nanotubes with selected diameters, lengths, chiralities, and orientations in a cost-effective manner, and to simultaneously optimize the kinetics, thermodynamics, and capacity of hydrogen adsorption on these materials. The long-term goal is to scale-up production of optimized materials to enable efficient, ambient temperature and pressure adsorption of hydrogen at energy densities specified by the Hydrogen Program Plan (6.5 wt % and 65 kg/m<sup>3</sup>).

#### **Task 1: Optimizing and Characterizing H<sub>2</sub> uptake and discharge**

NREL plans to study the effects of employing different metal hydrides such as Ti-Fe, Ti, Mg and Pd to assist the hydrogen adsorption process on SWNTs. These agents will be incorporated by methods that are more controllable than ultrasonication, and may be incorporated after synthesis of the SWNT materials via mechanical or chemical means, or directly during synthesis. In all cases, we will be paying careful attention to the intimacy of the SWNT/metal contact and to the metal particle sizes. To measure the degree of effectiveness, we will perform temperature programmed desorption and volumetric measurements to determine capacities, and probe the nature of the charge transfer mechanism with in situ-Raman investigations and conductivity measurements. A greater understanding of the activation process should enable to devise methods to scale-up the production of high-capacity hydrogen storage materials.

#### **Task 2: Nanotube Production, Purification, and Characterization**

Work this year will continue to explore the identities of particular tubes which give rise to the highest hydrogen adsorption capacity.

NREL will continue to investigate CVD-based growth with a focus on (1) developing a detailed understanding of the fundamental mechanisms and (2) developing methods to scale-up the CVD production to produce multi-gram and perhaps kilogram quantities of SWNTs. The tubes contained in these CVD samples are inherently different in size, type, and quality than those produced by laser vaporization, and these characteristics will be assessed. Also, NREL will explore the degree to which SWNT identities may be tuned by CVD. The purification technique developed for laser-grown materials will be applied to the CVD materials and adapted as required. These samples will be used in the hydrogen storage work described in Task 1, and be supplied to collaborators. The behaviors and characteristics of CVD and laser materials will be compared.

The synthesis work will require substantial characterization to assess the dimensions, chiralities, and quality of the SWNTs. Raman spectroscopy, infrared spectroscopy, thermal gravimetric analysis, and transmission and atomic force microscopies will be used extensively.

**Carbon Nanotube Materials for Hydrogen Storage**  
**National Renewable Energy Laboratory**

Task Designation/Milestone		FY2002					2003
		Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4	Qtr 1
<b>Task 1: Optimizing and Characterizing H<sub>2</sub> uptake and discharge</b>							
Explore methods to activate high-capacity hydrogen storage in SWNT samples by a process which differs from the incorporation of Ti-6Al-4V alloy by sonication and is more amenable to scale-up				◆			
<b>Task 2: Nanotube Production, Purification, and Characterization</b>							
Produce 100 mg samples of SWNTs by chemical vapor deposition						★	

FY2002 Begins October 1, 2001

★ = Critical Milestone

◆ = Milestone

## **Doped Carbon Nanotubes for Hydrogen Storage – Westinghouse Savannah River Technology Center**

The ultimate goal of this research is to develop a low-cost hydrogen storage material that has high capacity and is stable with cycling. It is expected that this material will possess favorable thermodynamics and kinetics characteristics compatible with the DOE goal for on-board hydrogen storage for transportation applications. Current approaches to hydrogen storage are compressed gas, liquid, or in the form of solid hydrogen. A solid hydrogen storage system is reliable, simple to engineer, and tremendously safer. Examples of solid hydrogen storage are metal hydrides, carbon (nanotubes, Fullerenes and activated carbon) or glass microspheres. Extensive research activities in the US and elsewhere have been exploring the use of carbon nanotubes for hydrogen storage.

Carbon nanotubes technology represents a new opportunity for solid hydrogen storage especially if these materials can store larger amounts of hydrogen at room temperature than graphite alone. Preliminary reports on hydrogen uptake and release by carbon nanotubes systems created much excitement and stimulated extensive interest in their potential use as hydrogen storage media. Yet hydrogen storage based on carbon nanotubes has not matured to a final product.

This project, however, is based on a different approach in developing carbon nanotubes capable of storing hydrogen. The unique nanotube structure and configuration can give rise to polarization and condensation that allows for hydrogen gas to be stored in the material. Controlled doping with nanoparticles is expected to facilitate the polarization and condensation of hydrogen in the tubes or between the tubes in a bundle of nanotubes. Controlling the type and size of the nanoparticle clusters is expected to allow for tuning the material for hydrogen sorption at desired temperatures and pressures. Large samples with consistent structures and characteristics must be produced for any results to be representative of a realistic hydrogen storage system. Methods of producing carbon nanotubes systems for hydrogen storage must take economics into consideration.

Fundamental study of the mechanism by which hydrogen can be stored in nanotubes is needed. Simple mechanisms for hydrogen uptake and release involving physisorption and chemisorption cannot account for the unusual uptake of hydrogen reported by other researchers. The Savannah River Technology Center (SRTC) believes that the unique nanotube structure and configuration can give rise to polarization and condensation inside the tubes. They believe that introducing nanoparticles (dopant) can enhance this mechanism at the edge and inside the tubes allowing for hydrogen storage to occur.

SRTC's approach has been defined along parallel but integrated tasks: material synthesis, thermodynamic characterization and fundamental study of mechanism using elemental and spectroscopic analysis.

### **Task 1: Synthesis of material**

Synthesis of doped nanotubes samples will be conducted. The synthesis of the doped nanotubes will be continued using a new technique we developed. Several materials will be used as dopants and large samples of nanotubes will be produced.

1a: Synthesize tubes with different dopants

1b: Synthesize tubes with different quantities of dopants

1c: Synthesize tubes with different diameters and configurations

### **Task 2: Thermodynamic and energetic characterization of hydriding/dehydriding**

In order to determine the performance of these carbon nanotube systems preliminary Thermal Desorption Spectrum (TPD) will be conducted followed by measurements performed using thermovolumetric system.

The rate of hydriding and dehydriding will be obtained at fixed temperatures and pressures. The stability of the doped nanotubes with cycling will be determined.

2a: Set up a high-pressure thermovolumetric system

2b: Continue hydriding and dehydriding measurements

2c: Examine nanotubes with cycling

### Task 3. Material Characterization and Elemental Analysis

The final product will be characterized using spectroscopy to assure high yield of pure material.

Elemental analysis of the product will be conducted. The subsequent hydriding and dehydriding cycles will be monitored in parallel with elemental and spectroscopic analysis. Hydrogen interaction with the nanotubes via uptake and release will be examined using spectroscopic techniques such as FTIR

3a: Spectroscopic analysis of product

3b: Spectroscopic analysis of cycled samples

3c: Spectroscopic analysis of hydrogen reaction with samples

Doped Carbon Nanotubes for Hydrogen Storage Savannah River Technology Center						
Task Designation/Milestone	2002					2003
	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4	Qtr 1
<b>Task 1. Synthesis of material</b>						
1a. Tubes with different dopents	◆	◆	◆	◆	◆	◆
1b. Tubes with different quantities of dopents		◆	◆	◆	◆	◆
1c. Tubes with different diameters and configurations					◆	◆
<b>Task 2. Thermodynamic characterization</b>						
2a. Set up a high pressure thermovolumetric system	◆	◆				
2b. Continue hydriding and dehydriding measurements	◆	◆	◆	◆		
3b. Examine nanotubes with cycling		◆			★	◆
<b>Task 3. Material analysis</b>						
3a. Spectroscopic analysis of product		◆	◆	◆		
3b. Spectroscopic analysis of cycled samples					◆	
3c. Spectroscopic analysis of H <sub>2</sub> reaction with samples					★	◆

FY2002 Begins October 1, 2001      ★ = Critical Milestone      ◆ = Milestone

## **Hydrogen Storage in Metal-Modified Single-Walled Carbon Nanotubes – California Institute of Technology**

Onboard hydrogen storage for transportation applications is a challenging problem from both scientific and engineering standpoints. Too many materials, including carbon nanofibers and single-walled nanotubes (SWNTs), generated initial excitement but ultimately fell short of the requirements of automotive engineering. In fact, many of these materials have also failed to show reproducible adsorption/desorption behavior in the laboratory, the hallmark of scientific legitimacy.

California Institute of Technology (Caltech) has performed experimental work in the area of hydrogen sorption in SWNTs and has measured the highest weight percentage of hydrogen storage capacity in a carbon that can be justified by thermodynamics, but only under the conditions of both low temperatures and high pressures (~8 wt% at 77K and 70 bar). Unfortunately, these conditions for high hydrogen storage capacity are far from engineering practicality. If the requirement of low temperature can be overcome, these SWNTs would be practical hydrogen sorbents.

Caltech proposes to investigate potassium and nickel as additions to SWNTs. It has been known for over thirty years that potassium-intercalated graphites can readily adsorb and desorb hydrogen at ~1 wt%. These levels are much higher than can be attained in pure graphite, owing to a larger thermodynamic enthalpy of adsorption. This increased enthalpy allows hydrogen sorption at higher temperatures. Potassium has other beneficial effects that enable the design of a new material:

- Increased adsorption enthalpy in potassium-intercalated graphite compared to pure graphite reduces the pressure and increases the temperature required for a given fractional coverage of hydrogen adsorption. Caltech expects the same effects in potassium-intercalated SWNTs.
- As an intercalant, potassium separates c-axis planes in graphite. Potassium also separates the individual tubes of SWNTs ropes producing swelling and increase surface area. Increased surface area provides more adsorption sites, giving a proportionately higher capacity.

### **Task 1: Synthesize SWNTs at Duke University and Purchase SWNTs from Carbon Nanotechnologies.**

Materials required for this work will be synthesized by Jie Liu's Group at Duke University. In addition, a commercial source of SWNTs will be used for this study. Carbon Nanotechnologies, a company founded by Rick Smalley of Rice University, pioneer in the synthesis of SWNTs, has both CVD and Laser-oven produced material, both of which Caltech will use in this study.

### **Task 2: Characterize SWNTs by N<sub>2</sub> BET Surface Area**

Initial surface area measurements via BET analysis will be performed to determine subsequent changes to surface area as a result of intercalation.

### **Task 3: Evaluate Tube Size Distribution Using TEM Analysis**

Caltech expects the tube size distribution to vary for the CVD prepared material. They also expect the Laser-oven material to have a narrow size distribution. Caltech will determine these using transmission electron microscopy (TEM).

### **Task 4: Evaluate Sorption Properties of As-Received Materials**

Caltech will use a Sievert's apparatus to determine hydrogen sorption properties of as-received materials.

**Task 5: Study and Optimize Intercalation Techniques for K Intercalation of SWNT Materials, Starting with Activated Carbon and Graphite**

Before attempting to intercalate SWNT materials, Caltech need to understand the intercalation of more common graphitic materials. They will develop the techniques for K intercalation into activated carbon and graphite in order to understand and optimize our procedures. They will begin with standard 2-zone furnace techniques for intercalation and move on to high pressure synthesis techniques using a Tetrahedron Press.

**Task 6: X-ray Diffraction and TEM Analysis of Intercalated Activated Carbon and Graphite Materials**

Caltech will characterize the graphitic materials using x-ray diffraction and TEM. This will be a necessary step as we expect K intercalated SWNTs to be air-sensitive and our handling and characterization procedures can be carried out on less valuable material, but material against which previous results in the literature can be compared.

**Task 7: Study Sorption Properties of these Materials in Order to Establish Suitable Baselines for Subsequent Studies**

Once Caltech is satisfied with their materials handling procedures, they will begin to carry out sorption measurements, which they will compare to literature values.

**Task 8: Optimize Intercalation Techniques with SWNTs**

Having tested out materials handling procedures on graphitic carbons, Caltech will apply their intercalation procedures to SWNT materials.

**Task 9: Determine Surface Area of Intercalated SWNTs**

BET analysis will be performed in order to determine the efficacy of K intercalation in increasing the surface area of SWNTs

**Task 10: Study Sorption Properties of SWNT Materials I Order to Establish Optimal Degree of Intercalation**

A Sieverts apparatus will be used to measure adsorption properties of the intercalated SWNTs and the results will be compared to our previous data. Caltech will measure isotherms at both LN2 and RT to test whether their hypothesis as to whether K intercalation should change the adsorption enthalpy of SWNTs.

**Task 11: Evaluate Materials Performance for Both Gravimetric and Volumetric Density**

Caltech will assess their data to determine the potential and utility of intercalated SWNTs as a sorbent for hydrogen storage. They will begin to evaluate the effectiveness of the Tetrahedron press as a synthesis technique for intercalating SWNTs.



### Hydrogen Storage in Metal-Modified Single-Walled Carbon Nanotubes California Institute of Technology

Task Designation/Milestone	2002					2003
	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4	Qtr 1
<b>Single Walled Nanotube (SWNT) Procurement</b>						
Procurement from carbon nanotechnologies		◆				
Synthesis at Duke and delivery to Caltech		◆				
<b>Characterization of as-received SWNT</b>						
Tube size distribution via transmission electron microscopy		◆				
X-ray diffraction (XRD) of as-received material		◆				
Brunauer-Emmett Teller (BET) surface area analysis		◆				
Iso-therms of as-received materials			◆			
<b>Intercalation of carbons</b>						
K intercalation of activated carbons and graphites			◆			
K intercalation of SWNTs				◆		
Optimization of intercalation procedures				★		
<b>Characterization of intercalated SWNT</b>						
X-ray diffraction of intercalated materials				◆		
BET surface analysis of intercalated material				◆		
<b>Gravimetric and volumetric density evaluation</b>						
Isotherms of intercalated materials					★	

FY2002 Begins October 1, 2001



= Critical Milestone



= Milestone

## METAL HYDRIDES

### Catalytically Enhanced Hydrogen Storage Systems – University of Hawaii

Methods have been developed for doping sodium aluminum hydride,  $\text{NaAlH}_4$  with titanium and/or zirconium such that: 1) rapid dehydriding occurs at temperatures as low as  $100^\circ\text{C}$ ; 2) rehydriding can be accomplished in only 15 minutes; and 3) 4.5 weight percent hydrogen can be repeatedly cycled through dehydriding/ rehydriding. Thus the doped materials hold great promise as hydrogen carriers for onboard fuel cells. However, further catalyst development is required in order for these materials to achieve commercial viability.

The PCP pincer complex,  $\text{IrH}_2\{\text{C}_6\text{H}_3\text{-2,6-(CH}_2\text{P}^t\text{Bu)}_2\}$  is the first reported homogeneous catalyst for the dehydrogenation of cycloalkanes to arenes. Unlike the heterogeneous catalysts for this reaction, it shows appreciable activity at low concentrations at temperatures as low as  $100^\circ\text{C}$ . The pincer complex also catalyzes the hydrogenation of arenes to cycloalkanes under moderate (10 atm) pressures of hydrogen. The two-way, hydrogenation/dehydrogenation activity of the catalyst suggests its application in a hydrogen storage system. Such a system meets the criteria of low cost and high hydrogen density (~7.0 wt %) required for a practical hydrogen storage system. The major drawback of a system based on cycloalkanes and the PCP pincer catalyst is that pronounced product inhibition occurs after about 10% dehydrogenation of cycloalkanes. Thus an improved catalyst must be developed.

#### **Task 1: Determination of Minimum Catalyst Doping Levels Required for Practical Hydrogen Storage Performance of $\text{NaAlH}_4$**

During the initial dehydriding reaction seen in equation 1,  $\text{NaAlH}_4$  rapidly evolves



hydrogen at moderate temperatures upon doping with 2 mole percent  $\text{Ti}(\text{O}^n\text{Bu})_4$  by methods of researchers at the University of Hawaii (UH). At  $100^\circ\text{C}$ , hydrogen flow rates of  $0.01 \text{ g H}_2/\text{s}$  per kg under a constant pressure of 1 atm. This dehydriding performance is adequate to meet the demands of a fuel cell operating under practical conditions. UH has also found that NaH and Al doped with 2 mole percent  $\text{Zr}(\text{O}^n\text{Pr})_4$  absorbs 4.4 weight percent hydrogen within 15 at  $120^\circ\text{C}$  under 125 atm of hydrogen. However, despite this progress in maximizing the catalytic enhancement of both the dehydriding and rehydriding process, it has not yet been demonstrated that ~5 weight percent hydrogen can be reversibly released from these materials under conditions that are required for the practical operation of an onboard fuel cell. Most notably, the rates of the second dehydriding reaction, seen in equation 2, and the reverse, hydriding of NaH



and Al to  $\text{NaAlH}_4$ , are impractical for hydride that is doped with titanium. UH found the rates of the second dehydriding reaction and its reverse are improved upon doping the hydride with zirconium. Their studies also indicate that the titanium and zirconium catalysts can act in concert to yield a material with an adequately enhanced kinetic performance over the course of the complete dehydriding reaction sequence and its reverse. However, the requirement of dual catalysts significantly affects the cyclable hydrogen weight percentage of the hydride. Therefore, the contribution of the transition metal dopant to the weight of the material must be minimized. During the next year of this project, efforts will be directed towards the milestones of determining the minimum levels of titanium and zirconium loadings that are required for adequate kinetics of  $\text{NaAlH}_4$  under the practically relevant conditions. Dehydriding studies will be

carried out at 100 °C under positive pressures (1-2 atm) of hydrogen. Rehydriding will be carried out at 100 °C under 100 atm of hydrogen.

## **Task 2: Solid State Nuclear Magnetic Resonance Spectroscopic Studies**

In collaboration with Prof. K. Kumashiro and Dr. W. Niemczura of the UH Department of Chemistry, the doped hydrides have been examined by solid state  $^1\text{H}$ ,  $^{27}\text{Al}$ , and  $^{23}\text{Na}$  NMR spectroscopy. These studies have allowed them to directly observe and quantify the different species that are present during the dehydriding and rehydriding processes. Additionally, the  $^1\text{H}$  NMR studies have led to the discovery that doping  $\text{NaAlH}_4$  greatly increases the proportion of mobile hydrogen in the **bulk** of the hydride. Thus the effect of the dopant on reducing the energetic barrier to the activation of hydrogen in the hydride can be quantified. UH plans to continue their solid state NMR studies of the effect of transition metal doping on the reversible dehydriding of  $\text{NaAlH}_4$ . These efforts will be directed toward the milestone of determining the activation parameters of the fundamental hydrogen dissociation process. The relative population of mobile hydrogen in undoped, titanium doped, and zirconium doped hydride will be quantified at temperatures ranging from 20-150 °C and activation parameters will be calculated from this data. UH also plans to prepare bulk quantities of the catalytically active species through the stoichiometric reaction of  $\text{NaAlH}_4$  with catalyst precursors. They will then characterize the materials that are produced through solid state  $^1\text{H}$ ,  $^{27}\text{Al}$ , and/or  $^{23}\text{Na}$  NMR spectroscopy. They hope to determine the identity of the active catalyst through comparison to the spectra of samples of titanium and aluminum compounds that will be purchased or prepared through established literature methods. These studies should allow UH to achieve the critical milestone of characterizing the enigmatic species that is responsible for the enhanced dehydriding and rehydriding kinetics of the doped hydrides.

## **Task 3: Testing of the Arsino Pincer Catalyst for Reversible Dehydrogenation of Alkanes**

UH has successfully synthesized the bis(arsino) pincer complex,  $\text{IrH}_2\{\text{C}_6\text{H}_3\text{-2,6-(CH}_2\text{AsBu}^t\text{)}_2\}$ . The complex catalyzes the dehydrogenation of methylcyclohexane to toluene. The dehydrogenation reaction proceeds to >20% conversion. This is a substantial improvement over 10 % conversion limit that is observed for the bis(phosphino) pincer catalyst. This result verifies our hypothesis that the  $\sigma$ -donor strength of the ligand greatly influences the attainable conversion level in the catalytic system. Unfortunately, it seems unlikely that UH will be able to adjust the methylcyclohexane/toluene system such that practically significant (>90 %) conversions can be attained. It is conceivable that the increasing steric bulk of the arene product would lower its affinity for the iridium center. Therefore, the product inhibition of the catalytic activity caused by product coordination in the case of toluene might not occur with larger arenes such as naphthalene and biphenyl. Guided by this hypothesis, UH will extend their studies of the bis(arsino) pincer catalyst to the further milestone of determining its dehydrogenation activity with larger cycloalkanes including decalin and dicyclohexyl.

Catalytically Enhanced Hydrogen Storage Systems University of Hawaii						
Task Designation/Milestone	2002					2003
	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4	Qtr 1
<b>Determination of Required Doping Levels</b>						
Determination of Ti level required for dehydriding of NaAlH <sub>4</sub>			◆			
Determination of Zr level required for hydriding of NaH/Al			◆			
Determination of Zr level required for dehydriding of Na <sub>3</sub> AlH <sub>6</sub>				◆		
<b>Solid State NMRS Studies</b>						
Determination of activation parameters				◆		
Identification of species responsible for kinetic enhancement					★	
<b>Evaluation of Bis(arsino) Pincer Catalyst</b>						
Determine maximum percent conversion of decalin and dicyclohexyl to naphthalene and biphenyl			◆			

FY2002 Begins October 1, 2001      ★ = Critical Milestone      ◆ = Milestone

## **Hydrogen Storage Development – Sandia National Laboratories**

The purpose of this project is to develop and demonstrate improved hydride storage materials for fixed site, infrastructure and transportation uses. This project is integrated into Sandia's overall hydrogen utilization program, but also includes (a) collaborative efforts with other hydrogen program participants, (b) other university and industrial partners to demonstrate storage system integration with fuel cells and other applications, and (c) participation in International Energy Agency Annex 17. The IEA work provides a mechanism for collaborating with researchers in Canada, Europe and Japan, and an international overview to the state-of-the-art in hydride development. Sandia has also participated in the Hydrogen Program educational outreach activities and plans to continue supporting these efforts.

The work has three main objectives: (1) the development of improved hydride materials, particularly lighter weight hydrides for vehicular applications, (2) developing state-of-the-art hydrogen storage/delivery and fuel cell systems integration, and (3) providing advanced materials and systems to engineering and industrial collaborative programs for eventual commercialization.

This year, the project is organized into the following three tasks:

### **Task 1: Light Weight Hydride Development.**

The goal of this task is to develop and demonstrate the next generation of practical hydrogen storage materials. Sandia's performance targets for rates and capacity derive from the requirements of PEM fuel-cell vehicles. Thus, their near term objective is a compact, lightweight, hydride capable of storing 5.5 wt.% H<sub>2</sub> (hydride only) that can be desorbed in less than 1 hour at 100°C. The long-term objective is the development of advanced materials and containment systems that deliver greater than 6 wt.% H<sub>2</sub> (system) at below 100°C in a safe and economically competitive manner. The application of the same materials for large-scale stationary hydrogen storage as well as small portable power-systems will also be evaluated.

This task will focus on modified complex metal hydrides. The work is based on achievements already gained in developing advanced Ti-doped NaAlH<sub>4</sub>. Those efforts produced processing methods and hydrocarbon-free dopants that nearly doubled the reversible hydrogen capacity and improved the hydrogen absorption and desorption rates by a factor of more than 10.

#### **Approach:**

Sandia will employ a parallel approach to hydrogen storage materials development by engaging in the following areas:

- A) *Testing new complex hydrides to achieve higher capacities.* This work was initiated last fiscal year as a collaboration with the University of Geneva which has provided samples to Sandia of newly synthesized complex hydrides. This collaboration is a result of participation in the International Energy Agency's Annex 17. Our IEA work provides a mechanism for collaborating with researchers in Canada, Europe and Japan, and an international overview to the state-of-the-art in hydride development.
- B) *Developing new methods to synthesize the complex hydrides and improve the doping process.* This is necessary to improve both rates and capacity and ultimately to reduce production costs. Sandia will continue to improve on our solvent-free direct-synthesis and doping process. They intend to investigate new approaches that bypass the current mechanical milling technique.
- C) *Characterizing material properties.* This will provide insight into the physical and chemical mechanisms of hydrogen release and absorption in order to make further advances in light weight

storage materials. Advanced materials will be characterized at our facility using volumetric Sieverts measurements, Arrhenius analysis, long-term cycling, XRD, SEM, TEM, XPS, Auger, GC/MS, TPD and thermal conductivity measurements. Neutron scattering and diffraction studies will be performed through collaborations with researchers at NIST. This work is closely coordinated with the University of Hawaii efforts in developing a fundamental understanding of alanate behavior.

- D) *Evaluating the performance of our materials on an engineering scale.*** This is required to ensure that they are on track for scale-up to commercialization. A scaled up test bed (100g) will be employed which provides, among other things, important information on the thermal transport and temperature excursions that may be expected in an operational complex hydride bed for fuel cell vehicle applications.
- E) *Studies of material safety issues associated with complex hydride storage systems.*** This is an important aspect of these new materials which needs to be addressed. Sandia intends to perform materials compatibility tests which include the effect of long-term cycling of Ti-doped NaAlH<sub>4</sub> together with typical container vessel materials. Materials safety studies of Ti-doped NaAlH<sub>4</sub> will be performed through a sub-contract with Thiokol Propulsion.

## **Task 2: IEA Annex 17**

The first experts workshop of this new annex was held in July 2001 following the completion of Annex 12. This new annex includes all advanced materials currently under investigation for storage applications. The IEA work provides a mechanism for collaborating with researchers in Canada, Europe and Japan, and an international overview to the state-of-the-art in storage development. This task consists of the following sub-tasks:

**A) *Operating Agent for Annex 17***

Dr. Gary Sandrock, SunaTech, Inc., is acting as operating agent for this annex. Sandia provides Dr. Sandrock with the required resources to perform this task.

**B) *Online materials database – Proj. H1***

This database server is a unique, powerful and accessible source of information on state-of-the-art storage materials, material properties and worldwide research activities. This years activities will be to expand the online databases as well as maintaining the server and upgrading system requirements when needed. The principal investigator on this project is Dr. Gary Sandrock.

**C) *Catalytically mod. hydriding properties of complex hydrides – Proj. H-10***

During this fiscal year, this work will investigate Ti catalysts on two complex hydrides prepared by K. Yvon, Univ. of Geneva. The principal investigator on this project is Dr. Karl Gross.

**D) *Engineering properties of new storage materials – Proj. HC-8***

With the current rapid development occurring with new storage materials, it is important to determine their engineering properties in order to implement their use in storage systems. This project will examine the engineering properties of complex hydrides and carbon materials. It is divided into two areas: (1) determination of the engineering properties of materials and, (2) parametric modeling of bed designs incorporating the new materials. The principal investigator on this project is Dr. George Thomas, consultant.

## **Task 3: Educational Outreach.**

Sandia will continue to participate in demonstrations at schools and at teachers' workshops as needed by the educational outreach coordinator. This year, we participated in the 5<sup>th</sup> Annual NHA Secondary

School Invitational in Washington, DC and also made presentations at a school workshop in California. Sandia will also continue to maintain the fuel cell powered car supplied to the educational outreach coordinator in 1999 through periodic maintenance and repairs as needed.

Hydrogen Storage Development Sandia National Laboratories						
Task Designation/Milestone	FY2002					2003
	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4	Qtr 1
<b>Hydride Development</b>						
Evaluate first complex materials			◆			
Complete safety tests				★		
Fabricate engineering bed 3					◆	
<b>IEA Annex 17</b>						
Experts meeting			◆			
Complete NaAl system						◆
FY2002 Begins October 1, 2001      ★ = Critical Milestone      ◆ = Milestone						

**Hydrogen Storage in Alanates – United Technologies Research Center**

Several catalysts from different groups that belong to transition, noble, and lanthanide elements will be introduced to the hydride material in an attempt to enhance the kinetics of hydriding/dehydriding. The catalysts will be introduced, using organometallic compounds or transition metal salts that contain these elements or directly introduce the elements by ball milling techniques. UTRC will consult with program managers of other projects on analysis and characterization of catalyzed material.

*This project is currently being negotiated.*



## **Complex Hydrides for Hydrogen Storage – Florida Solar Energy Center**

The goal of this project is to investigate complex hydrides as hydrogen storage materials. These compounds, sometimes referred to as chemical hydrides, were previously not known to be reversible. Recent reports in the literature, however, have shown that sodium aluminum hydride ( $\text{NaAlH}_4$ ) can be reversibly dehydrided. While  $\text{NaAlH}_4$  contains 7.5-weight percent (wt%) hydrogen, only 4 wt% is reversible using the previously studied catalysts. For serious consideration for mobile applications, a hydrogen storage material must be capable of an installed hydrogen density of at least 5.5 wt%.

Florida Solar Energy Center (FSEC) will investigate a series of complex hydrides of aluminum and/or boron, with large hydrogen contents, a minimum of 7.5% by mass. Specifically, the initial compounds to be studied will include  $\text{LiAlH}_4$ ,  $\text{LiBH}_4$ ,  $\text{Al}(\text{BH}_4)_3$ ,  $\text{LiAlH}_2(\text{BH}_4)_2$ ,  $\text{Mg}(\text{AlH}_4)_2$ ,  $\text{Mg}(\text{BH}_4)_2$ ,  $\text{Ca}(\text{AlH}_4)_2$ ,  $\text{Ca}(\text{BH}_4)_2$ ,  $\text{NaAlH}_4$ ,  $\text{NaBH}_4$ ,  $\text{Ti}(\text{BH}_4)_3$ ,  $\text{Ti}(\text{AlH}_4)_4$ ,  $\text{Zr}(\text{BH}_4)_3$ , and  $\text{Fe}(\text{BH}_4)_3$ . Some of these materials are available commercially and will be obtained from the supplier for initial testing. Methods for synthesizing the others are available in the literature or will be worked out during the study.

The complex hydrides first will be examined in their pure form for hydrogen release and uptake characteristics. After establishing these baseline measurements, each will be subjected to catalyst loading and retested. The catalysts to be utilized will contain titanium, in the forms  $\text{TiCl}_4$ ,  $\text{TiCl}_3$ , and  $\text{Ti}(\text{OBu})_4$ ; iron as  $\text{FeCl}_3$ ; zirconium as  $\text{Zr}(\text{OPr})_4$ ; and carbon as graphite or activated carbon. Catalyst loading will be accomplished using both chemical and mechanical means.

Systems in which catalysts have an effect will be further investigated using x-ray photoelectron spectroscopy, auger electron spectroscopy, x-ray diffraction, scanning electron microscopy, and energy dispersive x-ray analysis. The purpose of these studies will be to determine the fate of the catalytic additives in order to surmise the mechanism of their actions. The information will be utilized to determine other catalysts that might be more effective than those studies.

### **Task 1: Acquisition of Compounds**

During the first three months of the contract, those compounds that are commercially available will be purchased. Literature references are available for the synthesis of those not commercially available and an extra two months is being allotted to the synthetic work. The literature procedures will be utilized as the starting point for producing each of these hydrides and modified as necessary.

### **Task 2: Determination of Hydrogen Uptake and Release Characteristics of each Compound in their Pure Forms**

The hydrogen thermovolumetric analysis instrumentation available at FSEC will be utilized to develop PCT curves for each compound. The temperature, pressure and enthalpy of the hydrogen uptake and release will be determined using a differential scanning calorimeter. This task will begin when the first compound is obtained and continued as long as new compounds are being prepared.

### **Task 3: Determine Effects of Catalysts**

Methods by which to incorporate the catalysts, particularly titanium, iron, zirconium and carbon, will be studied. Transition metal compounds will be incorporated in solution and mechanically. The influence of the catalysts on both hydrogen release and cycling will be determined. The following compounds will be studied for their catalytic effects on a pre-determined list of compounds: titanium, in the forms of  $\text{TiCl}_4$ ,  $\text{TiCl}_3$ , and  $\text{Ti}(\text{OBu})_4$ ; iron as  $\text{FeCl}_3$ ; zirconium as  $\text{Zr}(\text{OPr})_4$ ; and carbon as graphite or activated carbon. These will be studied individually and in all possible combinations.

#### Task 4: Gain Fundamental Understanding of the Mechanisms of the Actions of the Catalysts

Systems in which catalysts have an effect will be further investigated using x-ray photoelectron spectroscopy, auger electron spectroscopy, x-ray diffraction, scanning electron microscopy, and energy dispersive x-ray analysis. The purpose of these studies will be to determine the fate of the catalytic additives in order to surmise the mechanism of their actions. The information will be utilized in the final task.

#### Task 5: Determination of Additional Catalysts

The exact work performed in this task will be determined after Task 3 data is obtained. However, the initial approach consists of two parts. Part one will be the study of a series of metals and non-metals that can be added singly and in combination as potential catalysts. The second part will be to study the effects of systems, such as Ziegler-Natta catalysts, that might be effective catalysts.

Complex Hydrides for Hydrogen Storage University of Central Florida						
Task Designation/Milestone	2002					2003
	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4	Qtr 1
Acquire commercially available compounds		◆				
Synthesize reported compounds			◆			
Develop syntheses for unreported compounds				◆		
Determine H interaction properties of purchased pure compounds			◆			
Determine H interaction properties of synthesized pure compounds					◆	
Catalyst incorporation methods study				◆		
Determination of catalyst effects				★		
Catalyst mechanism study					★	
Propose and study of other catalysts						◆

FY2002 Begins October 1, 2001      ★ = Critical Milestone      ◆ = Milestone

## PHYSICAL STORAGE

### **Vehicular Hydrogen Storage Using Advanced Tanks – Lawrence Livermore National Laboratory and Idaho National Energy Engineering Laboratory**

#### **Overview**

Advanced composite hydrogen tanks are undergoing rapid evolution. Previous generations with advanced weight performance, pioneered at LLNL, are currently being commercialized. This proposal advances hydrogen tankage into a next generation, departing from incremental progress based on aerospace tank technologies of the 1970's.

Prototyping, modeling, and destructive testing is proposed that will affordably go beyond the current state-of-the-art in materials, processes, and mass-production cost. Quantities of small tanks must be built and burst to deliver statistical performance results sufficient to tailor new material and manufacturing techniques that have yet to be applied in tanks. This type of process improvement is known in the semiconductor industry as Process Research, and LLNL proposes to bring these methods to structural mass production for the first time.

Prototyping efforts that can affordably produce quantities of test articles could conceivably provide tanks for small demonstration vehicles in future years. Such tanks will be enabling for hydrogen fueled vehicles too small to be well served by any current storage technology. Some permeation results from tank testing may also support improved safety standards.

#### **Technical Description- LLNL**

Medium-term research is proposed that might merit commercialization in roughly three years. The proposed research has elicited vigorous interest from LLNL industrial partners, and should result in safer, denser, less expensive, as well as lighter weight hydrogen storage for vehicles of all sizes. LLNL is adding pursuit of fundamental cost improvements to its pursuit of safety comprehension and weight reduction. Cost improvement innovations proposed include continuing pursuit of more 'efficient' composite utilization and advances in thin liners, both of which the LLNL team has steadily innovated over the past three years. Other forecast cost improvements are anticipated from process and materials research that should establish the feasibility of blow molded liners. More than half of forecast cost improvements will come from safety innovations. The prospect of investigating a potential breakthrough in tank safety that might lead to benign burst failures is beyond the scope of this year's proposed research, but enabled by the affordable prototype tanks, facilities, and equipment anticipated in this proposal.

Roughly 20% of FY01 funding has been employed to design an affordable next generation tank. Most of FY01 funding was expended in support of vehicle demonstrations (that were beyond DOE's means to bring to successful fruition in the Summer of 2001). A survey of industrial partners' capabilities captured the current (threadbare) state of the art, and located the partners LLNL will need to prototype next generation tanks. The minimal effort sufficient to design molding contours (for expensive blow mold tooling) was performed, including netting analysis and classical lamination theory stress predictions. Proposed Tasks 1 through 3 will implement this design in the first half of FY02.

Task 4 will acquire burst pressure data from the quantity of small tanks produced in batches with varied process parameters. Two test sites are likely to provide measurements that can be cross-checked, one at LLNL and another in Colorado. Portable data acquisition equipment compatible with dirty operations in the field is under construction to support this multi-location test program. Task 5 will employ the same test facilities to acquire permeation performance data from tanks before they are burst, including the first

probe of a fundamental untested phenomenology – permeation degradation with cycling. Task 6 continues liner innovation research with the first attempt at implementing permeation barrier coatings on liners themselves, not liner material coupons. Task 7 collects and analyzes the statistical burst data from Task 4 to seek improved manufacturing process parameters, and should demonstrate the feasibility of LLNL's approach to more 'efficient' use of expensive composite material.

**Tasks/Milestones:**

Task 1: Produce blow mold tooling for next generation of small vehicular hydrogen tankage.

Task 2: Blow mold large quantity (~200) of experimental tank liners capable of unwound pressurization.

Task 3: Wind a statistically significant quantity (25, 5 batches of 5) of experimental tanks.

Task 4: Burst test new generation hydrogen tankage to affordably continue probing the PbV/W frontier.

Task 5: Perform integrated pressure vessel leak tests to investigate permeation degradation with cycling.

Task 6: Coat liners' curved surfaces under pre-stress to demonstrate 'tempered' permeation barriers.

Task 7: Use burst test statistics from experimental tanks to enable tank manufacturing process research.

**Technical Description- INEEL**

INEEL will develop an electrochemically "active" hydrogen barrier, fabricated from polymers. This barrier will have the following features:

- (a) The barrier will be constructed of three layers of polymers consisting of a proton-conducting electrolyte (electronic insulator) sandwiched in-between electronically conductive polymers (electrodes). The electrodes need to be slightly porous and/or exhibit significant hydrogen solubility/permeability; however, most polymers meet this requirement.
- (b) The layers will be manufactured in-situ from dip coating or spraying of monomers that are later polymerized. Since all the layers are polymers they are flexible with elastic modulus that is equal or less than that of the underlying polymer (e.g. cross-linked polyethylene).
- (c) The device will be a galvanic type device (very low current) that requires application of a small dc voltage (e.g. from a battery).
- (d) The hydrogen partial pressure established by the voltage is extremely low at the underlying polymer interface. The hydrogen partial pressure can be calculated using the Nernst equation.

**Tasks:****Task 1: Selection of materials**

Two basic polymers will be selected: (a) a proton conducting electrolyte, (b) electronically conductive electrodes. It is required that the materials be fabricated in-situ by polymerization (curing) of dip-coated or spray-coated monomers. The electrolyte does not need high proton conductivity, but it has to be a proton conductor when it is "dry" and thus cannot exclusively be a hydrated hydronium conductor (e.g. nafion).

**Task 2: Fabrication of the tri-layer coatings**

Both “dip” and spray coating of appropriate monomers will be investigated. Polymerization (curing) methods will be engineered (based upon the chemistry of the monomers). Good bonding and pinhole free electrolyte layers are the goals.

**Task 3: Experimental verification of hydrogenation protection**

Small (sub-scale) experimental hydrogen gas storage “bottles” with plastic liners will be fabricated. Hydrogen permeability measurement methods will be developed for the experimental “bottles”. Permeability rates for “bare” plastic liners will be compared to plastic liners protected with the new electrochemically active hydrogen barrier.

<b>Vehicular Hydrogen Storage Using Advanced Tanks</b> <b>Lawrence Livermore National Laboratory</b>						
Task Designation/Milestone	FY 2002					2003
	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr4	Qtr 1
Task 1. Liner Tooling			◆			
Task 2. Blow Mold Liners			◆			
Task 3. Wind Tanks				◆	◆	
Task 4. Burst Test Tanks				◆	◆	
Task 5. Integral Leak Test					◆	
Task 6. Non-Planar Coating				◆		
Task 7. Statistical Process Research				◆	★	

FY2002 Begins October 1, 2001      ★ = Critical Milestone      ◆ = Milestone

## **Advanced Thermal Hydrogen Compression – Ergenics, Inc.**

Ergenics is investigating the application of a novel thermal hydrogen compression process to hydrogen produced from renewable resources. The thermal compressor is an absorption-based system that uses the properties of reversible metal hydride alloys. Hydrogen is absorbed into an alloy bed at ambient temperature and is desorbed at elevated pressure when the bed is heated with hot water. Thermal compression offers a number of improvements over traditional mechanical compression in reliability, cost effectiveness and hydrogen purity, especially when compressing hydrogen to very high pressures of over 340 bar (>5,000 psi).

Hydrogen produced from renewable energy resources can contain impurities that a) can adversely affect fuel cell operation, b) might interfere with or do permanent damage to the new, high storage density materials under development, several of which absorb hydrogen only at elevated pressure and/or c) can damage the alloy in a thermal compressor. Ergenics has developed three processes that may permit hydride alloy beds to tolerate higher levels of impurities, in some cases up to 10,000 ppm or more. Passive Purification is used for water vapor and oxygen, Elevated Temperature Desorption is used for CO and CO<sub>2</sub>, and Automatic Venting can clear inert gas blanketing caused by N<sub>2</sub> and CH<sub>4</sub>. Employing these processes in a thermal compressor may allow simultaneous compression and purification, which resolves major system-level problems that could be encountered with new, high density storage materials and fuel cells.

Ergenics is designing and building a pilot scale thermal compressor that includes the three purification techniques and an associated test apparatus. The compressor will be tested on hydrogen containing various inlet impurity levels to determine threshold contamination levels (levels at which compressor performance is affected). Outlet impurity levels will be monitored to determine the effectiveness of compression-with-purification. Compressor performance to very high pressures will be demonstrated.

### **Task 1: Construct a single stage thermal compressor to verify performance with impure hydrogen.**

Design and build a single stage thermal compressor that includes a miniature hydride heat exchanger (0.125 inch diameter hydride bed), provisions for purification, hydrogen check valves, hot and cold water valves and associated components and controls.

### **Task 2: Assemble a thermal compressor test apparatus.**

Construct a test apparatus that will quantify compressor performance. The test apparatus includes a hot water heating sub-system, cold water sub-system and hydrogen monitoring sub-system.

### **Task 3: Test the thermal compressor (Critical Milestone)**

Determine compressor performance while processing hydrogen that contains impure gas species. Determine threshold contamination levels for H<sub>2</sub>O, O<sub>2</sub>, CO and N<sub>2</sub>. The tests will demonstrate the relationship between inlet and outlet impurity levels and hydrogen venting. Data from these tests will be used to determine the overall viability of using thermal hydrogen compression with renewable hydrogen production processes, new high-density storage materials, and various fuel cell processes.

### **Task 4: Develop a high pressure hydride alloy.**

Subtask 4.1: Engineer, melt and test hydride alloys suitable for compressor operation over 5,000 psig. Testing will include Pressure-Composition-Temperature (PCT) Isotherms of intermediate stage alloys as well as PCT testing of the last stage over 5,000 psi before and periodically during high pressure soaking.

**Subtask 4.2:** Select alloys suitable for the remaining compressor stages.

**Task 5: Investigate very-high-pressure containment options for components.**

Determine the availability of and/or containment options for particle filters, check valves and other components for very-high-pressure operation.

**Task 6: Validate the entire thermal compression-with-purification process.**

Construct additional stages for the pilot-scale 5,000 psig thermal compressor and test the system to validate performance predictions. The pilot scale compressor will process ~15 l/m, about the size required for overnight refueling of a hydrogen fueled automobile.

**Task 7: (clerical work and meeting attendance)**

**Task 8: Participate in IEA Annex 17**

Participate in IEA Annex 17, "Solid and Liquid State Hydrogen Storage Materials" with an engineering and demonstration project for compression-with-purification.

**Task 9: Summarize results in a Project Report.**

The project report will include a complete economic analysis comparing thermal compression-with-purification with mechanical compression. Suitability for use with different hydrogen production processes and new high-density storage materials will be evaluated.

Advanced Thermal Hydrogen Compression Ergenics, Inc.						
Task Designation/Milestone	FY 2002					2003
	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4	Qtr 1
Task 1: Build a single stage thermal compressor to verify performance with impure hydrogen.		◆				
Task 2: Assemble a thermal compressor test apparatus		◆				
Task 3: Test the thermal compressor			★			
Task 4: Develop a high pressure hydride alloy				◆		
Task 5: Investigate very-high-pressure containment options for components.				◆		
Task 6: Validate the entire thermal compression-with-purification process.					◆	
Task 8: Participate in IEA Annex 17						◆
Task 9: Summarize results in a Project Report						◆

FY2002 Begins October 1, 2001      ★ = Critical Milestone      ◆ = Milestone

### 3.1.3 Hydrogen Utilization Research Projects

Utilization of hydrogen as an energy source occurs typically either via an electrochemical process such as in a fuel cell or by a combustion process. In addition, the use of hydrogen necessitates the ability to detect its presence in the event of leaks. The Hydrogen Program effort also supports R&D in the area of hydrogen sensors. This section, summarized in Table 3.4, is categorized accordingly.

<b>Table 3.4</b> <b>Hydrogen Utilization Research</b>		
<b>Goal: Develop fuel cell and reversible fuel cell technologies as an efficient low-cost means of converting hydrogen into electric power.</b>		
<b>Category</b>	<b>Project</b>	<b>Researchers</b>
<i>Fuel Cells</i>	Fuel Cell and Electrolyzer Research, Development and Demonstration	Los Alamos National Laboratory
	Low Cost, High Efficiency, Reversible Fuel Cell System	Technology Management, Inc.
	Gallium Nitride Integrated Gas/Temperature Sensors for Fuel Cell System Monitoring for H <sub>2</sub> and CO	Peterson Ridge, LLC
	Design and Development of New NanoEngineering Glass-Ceramic Proton Conducting Membranes (GCPCMs) for High Performance H <sub>2</sub> -O <sub>2</sub> Proton Exchange Fuel Cells	Iowa State University
<i>Internal Combustion Engines/Turbines</i>	Internal Combustion Engines Research and Development	Sandia National Laboratories
	Reduced Turbine Emissions Using Hydrogen-Enriched Fuels	Sandia National Laboratories
	Hydrogen/Natural Gas Blends	NRG Technologies
<i>Hydrogen Safety</i>	Interfacial Stability of Thin Film Hydrogen Sensors	National Renewable Energy Laboratory
	Integrated Micro-Machined Hydrogen Gas Sensors	Advanced Technology Materials, Inc.
	Codes and Standards Analysis	University of Miami
	High Efficiency Steam Electrolyzer	Lawrence Livermore National Laboratory



## FUEL CELLS

### Fuel Cell and Electrolyzer Research, Development, and Demonstration – Los Alamos National Laboratory

**Issues In Accelerating Commercial Timetables.** Fuel cell development in the DOE has been focused in the Office of Advanced Automotive Technologies and, to a lesser degree, in the Fuel Cells for Buildings Program, both in the Office of Energy Efficiency and Renewable Energy. High-temperature fuel cell RD&D has been pursued by the Office of Fossil Energy. Smaller government-funded programs are run out of the Commerce, Transportation and Defense Departments. Existing programs have unresolved issues, particularly for hydrogen systems (the bulk of the current effort is targeted on “reformat” fuel cells, using hydrogen-rich gas streams reformed from liquid fuels for transportation and from natural gas or propane for distributed power).

**Cost.** First-generation product engineering is underway and technically viable products will be available this decade. Projected costs, however, remain non-competitive for broad market penetration. Significant cost reduction will require both performance improvement and materials substitution (an example being replacement of precious-metal catalysts). Current systems are far from simple, with complex subsystems required for reactant and water management, thermal control, freeze protection, etc. “Leap-frog” approaches that transcend the first-generation design paradigm are needed for significant cost reduction.

**Durability.** Current systems do not meet the durability needs for either automotive applications (about 4000 hours) or distributed power applications (40,000-50,000 hours) even in the development laboratory, and the real-world environment can be much harsher. Potential fuel cell manufacturers do not have the confidence in system durability to provide warranty protection and cannot confidently project support needs after lease or sale.

**Efficiency.** While efficiency of direct hydrogen systems is good, further improvement is possible and desirable. Automotive systems with on-board reformers need further efficiency improvement without relaxing cost and size constraints to be competitive with internal combustion engines.

The tasks presented below address the issues above and leverage existing expertise, capability and programs at the Los Alamos National Laboratory (LANL).

#### **Task 1: Enabling Science for Membrane-Based, Precious-Metal-Free Alkaline Fuel Cells**

A major drawback of polymer electrolyte fuel cells (PEFCs, also known as proton exchange membrane or polymer electrolyte membrane *PEM* cells) is the use of expensive precious metal catalysts in the electrodes, required to achieve reasonable catalytic rates at relatively low operating temperatures. There are questions surrounding cost and availability of the Pt used in these electrodes.

LANL proposes to carry out a research effort to enable a new generation of fuel cells based on alkaline electrolytes employing non-precious metals. Achieving the targets of this research would provide a scientific basis to revolutionize fuel cell cost and availability, introducing a cornerstone of the 21<sup>st</sup> century ‘hydrogen economy.’ Alkaline fuel cells (AFCs) allow substantially improved electrocatalysis, but have several technical drawbacks including difficulty of CO<sub>2</sub> rejection from the electrolyte and the use of liquid electrolytes, leading to relatively high resistive losses in practical devices.

LANL’s approach to overcoming the hurdles to realize AFC technology will rest on deep scientific understanding of the problems coupled to technological realism. Key areas of research that we will carry out to address present-day shortcomings include:

- Evaluate AFC technology status and assess alternate approaches and technical advances, leading to an R&D plan
- Conduction in new polymer-based alkaline electrolytes
- Improved electrocatalysis in alkaline systems

### **Task 2: Enabling Science for Advanced Ceramic Membrane Electrolyzers**

The principal goal of this project is to demonstrate electrolysis technology using ceramic electrochemical cells based on solid oxide proton conductors. Los Alamos has experience in solid-state bulk and thin film materials synthesis and characterization capability. We will synthesize and characterize electrolyte and electrode materials and fabricate test cell apparatus. Characterization methods available in the Electronic and Electrochemical Materials and Devices Group include XRD, TGA, EDAX, SEM and AC impedance and DC cyclic voltammetry electrochemical methods.

- Evaluate proton-exchange ceramic membranes for use in electrolyzers
- Fabricate dense ceramics of cerates and zirconates and measure the bulk hydrogen conductivity using AC impedance spectroscopy and DC conductivity measurements, demonstrate water electrolysis using these materials
- Synthesize electrode materials for electrolysis and characterize their polarization behavior using electrochemical methods

### **Task 3: A Rugged, Low-Cost Fuel Cell Power System for Personal Mobility Vehicles.**

- Complete characterization of commercial battery-powered Pride Victory scooter.
- Demonstrate rugged, low-cost single-cell/short-stack with required power density.
- Finalize design of scooter power system(s) and initiate build/testing /installation.
- Demonstrate a complete >200W “active” air-breather fuel cell system.

### **Task 4: Adiabatic Stack and System Development**

- Decrease stack component costs to 30% less than '01 costs.
- Demonstrate increase in power density of 50% over '01 status.

### **Task 5: Direct-Hydrogen Fuel Cell Power System Level Simulation**

Existing fuel cell power system models, notably GCTool developed by Argonne National Laboratory for the Office of Transportation Technologies, lack the fidelity needed to quantify design and operational tradeoffs in direct-hydrogen fuel cell power systems. In particular, there is no “design mode” where components are sized and where the implications and consequences of design tradeoffs can be determined. LANL proposes to adapt and enhance system-level models developed at Los Alamos in the 1990s for fuel cell power systems and for regenerative power systems, to allow a fresh look at system optimization. The Fuel Cell System code (FCSYS) developed during the General Motors Electrochemical Engine Project, and REGEN, a regenerative system code developed for NASA to study lunar-base power system options, combining solar photovoltaic systems with electrolyzers, storage and fuel cells, will be updated with the latest data and enhanced as necessary. Insights gained through years of fundamental research and reflected in the Los Alamos suite of fuel cell phenomena models will be appropriately incorporated in the system-level descriptions. The FCSYS and REGEN models not only calculate energy and mass flows, but also size components, estimating both weight and volume, associated with changes in system configuration. Efficiencies of each component, including motors, controllers, etc., are accounted for and the system-level impacts quantified. LANL will also obtain GCTool and improve the direct-hydrogen models therein.

This suite of models would be available for stand-alone use to help guide development and technology validation efforts. LANL would also work with the NREL analysis team to assure defensible assumptions are used in higher-level analyses.

<b>Fuel Cell Electrolyzer Research, Development and Demonstration</b> <b>Los Alamos National Laboratory</b>						
Task Designation/Milestone	FY2002					2003
	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4	Qtr 1
<b>Task 1. Enabling Science for Alkaline Fuel Cells</b>						
Report on technology assessment and document resulting R&D plan			◆			
Determine most promising polymer and gel electrolytes and synthesize test materials					◆	
Report on studies of electrode structure and non-noble metal catalysis					◆	
<b>Task 2. Enabling Science for Adv. Electrolyzers</b>						
Report on technology assessment and document resulting R&D plan			◆			
Determine most promising proton-conducting ceramic electrolytes and fabricate					◆	
<b>Task 3. Personal Mobility Vehicle Fuel Cell</b>						
Complete characterization of commercial battery-powered Pride Vistory scooter		◆				
Demonstrate rugged, low-cost single-cell/short stack with required power density			◆			
Finalize design of scooter power system(s) and initiate build/testing/installation			◆			
Demonstrate a complete >200W "active" air-breather fuel cell system					★	
<b>Task 4. Adiabatic Stack and System Development</b>						
Decrease stack component costs to 30% less than '01 costs					◆	
Demonstrate increase in power density of 50% over '01 status					◆	
<b>Task 5. Direct-Hydrogen Fuel Cell Power System Level Simulation</b>						
Complete initial phase code update and enhancement and initiate assessment analyses			◆			
Document updated code			◆			

FY2002 Begins October 1, 2001      ★ = Critical Milestone      ◆ = Milestone

## **Low Cost, High Efficiency, Reversible Fuel Cell Systems – Technology Management, Inc.**

Electric power systems based upon renewable power sources (chiefly solar, wind, and water) offer the potential for significantly reducing CO<sub>2</sub> emissions while offering superior siting flexibility and other advantages. However, the installed cost of a complete, grid-independent system can be very high. As an alternative, a single device operating reversibly as both fuel cell and electrolyzer, combined with renewable power, can enhance grid-independent or grid-augmented systems and greatly improve the quality, availability, and affordability of electric of power.

The high operating temperature of the solid oxide fuel cell (SOFC) allows several advantages over low temperature fuel cells (e.g., the polymer exchange membrane (PEM) cell) including:

- Significantly higher potential “round trip” energy storage efficiency
- Significantly higher fuel-to-electricity efficiency on common fuels
- Potentially lower costs with higher reliability.

Technology Management, Inc. has completed preliminary tests and engineering studies that show a reversible solid-oxide fuel cell/electrolyzer system is capable of:

- Storing electric energy generated from renewable sources at projected “round-trip” efficiencies over 80%
- Providing backup power generated from propane at lower heating efficiencies over 60%.

The system utilizes a single set of stacks for all electrochemical functions together with a system design that stores both gases and thermal energy. Experimentally\*, TMI has demonstrated high efficiency reversible operation of single cells at conditions that represent the average predicted environment and gas composition in a reversible system. Compared to state-of-the-art TMI SOFC designs, the cell area specific resistance (ASR) was about 10% higher for reversible cell designs, but is acceptable for early development. The best cells were operated in steady state (non-cycling) conditions for up to 2000 hours. This work is being actively extended to the full range of operating conditions predicted for cells and small stacks.

### **Scope of the Current Effort**

Reversible SOFC systems require the development of modified solid-oxide electrochemical stacks that include isolated passive fuel and oxygen flow circuits, complete gas isolation, and stable reversible operation. Two overall technical goals for the follow-on work include:

- Development and demonstration (reproducibly) of five-cell advanced fuel cell stacks operating on H<sub>2</sub>/H<sub>2</sub>O fuel mixtures (which simulate the oxygen potential of reformed propane) plus air with simulated lower heating value (LHV) efficiencies above 50% and aging rates below 5% per 1000 hours.
- Demonstration of five-cell advanced fuel cell stacks in reversible mode (alternating electrolysis and fuel cell operation) with simulated energy storage efficiencies above 70% and aging rates below 5% per 1000 hours.

The technical approach to meet these objectives includes reducing cell polarization by optimizing electrode and cell geometry, maintaining stable microstructures through temperature and compositional modifications, and assuring reproducible fabrication through mechanized manufacturing and inspection methods.

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\* Under funding from NASA SBIR Programs (1995-1998)

## Work Plan Summary

### Task 2: Stack Development and Testing

In early 2002, Technology Management, Inc. expects to demonstrate reversible operation in small stacks of 3-5 cells. Through 2001, all tests have been evaluated using conditions that represent average operating conditions. In 2002, tests will be conducted using a broader range of test conditions including some severe 'end point' conditions to explore the range of stable operations. Successful reversible testing represents the single most significant milestone and is important for all future efforts.

### Task 3: Revised Economic / Engineering Calculations

In 2002, a review of the economic and engineering analysis will be conducted. This will be based on the approach used in earlier studies but modified by the ongoing results from this follow-on phase. Boundary conditions will be re-evaluated and new learnings incorporated.

### Task 4: Report and Follow-on Proposal

TMI expects to complete the research program in 2002. A larger system will be proposed which demonstrates the technology at a larger scale and begins to incorporate thermal storage that have not been practical up to this point.

Low Cost, High Efficiency Reversible Fuel Cell Systems Technology Management, Inc.						
Task Designation/Milestone	FY2002					2003
	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr4	Qtr 1
Stack Development and Testing			★			
Revised Economic and Engineering Calculations				◆		
Reporting and Follow-on Proposals				◆		

FY2002 Begins October 1, 2001      ★ = Critical Milestone      ◆ = Milestone

## **Gallium Nitride Integrated Gas/Temperature Sensors for Fuel Cell System Monitoring for H<sub>2</sub> and CO – Peterson Ridge, LLC**

The electrodes in solid polymer electrolyte fuel cell systems require hydrogen fuel free from carbon monoxide (CO), or the platinum electrodes are poisoned and fuel efficiency is degraded. Steam reforming of hydrocarbon fuels produces a mix of hydrogen, carbon dioxide and enough by product CO to poison the electrodes. Preferential oxidation (PROX) of CO to reduce this contaminant is accomplished over a noble metal catalyst typically platinum by adding oxygen to the hydrogen fuel upstream of the PROX catalyst. An inexpensive monitor to confirm the PROX catalyst efficiency and ultimately control the PROX system conditions is useful if not necessary to avoid the risk that PROX catalyst degradation could lead to reduced fuel efficiency or failure of the fuel cell due to contaminated hydrogen. Since the environment for a PROX monitor is rich in hydrogen, the problem is developing a sensor sensitive enough to monitor carbon monoxide at high temperature without the sensor output being dominated by hydrogen or temperature.

Peterson Ridge is exploring an approach combining the advantages of the sensing capabilities of the catalytic metal gate with a wide bandgap GaN semiconductor metal semiconductor field effect transistor (MESFET) and modulation doped field effect transistor (MODFET) transducers for high temperature measurement of carbon monoxide in hydrogen. The choice of the catalytic metals for the device is based on the metals used in PROX reactors – namely platinum, palladium/silver and rhodium.

### **Tasks for FY2002**

#### **Task 1: Main effect testing**

Testing CO will be done in the lower range of 5-100ppm at temperatures up to 400C.

#### **Task 2: Interferent testing**

#### **Task 3: Fabrication, Testing and Refabrication Complete**

A long-term program of redesigning and fabricating sensors as well as laboratory testing will be concurrent with developing electronics and analysis software. A lack of manpower for fabrication at the University of Utah meant a delay in this milestone and dependent tasks (including tasks one and two) into FY2002.

#### **Task 4: Outsource 2nd Generation Fabrication**

A source has been identified. A contract has yet to be negotiated.

#### **Task 5: Product Development Plan**

Product development will involve fuel cell manufacturers who have shown an interest in the sensor. High Temperature Probe Assembly Complete

#### **Task 6: Alpha Prototype Design and Assembly**

The test articles including sensor probe, data acquisition and communication modules will be assembled and calibrated in the laboratory prior to installation in the field.

**Task 7: Prototype Reformer Test**

A local partner Idatech has agreed to host a test of the hardened prototype.

**Task 8: Prototype Redesign and Test**

**Gallium Nitride Integrated Gas/Temperature Sensors for Fuel Cell System Monitoring for  
Hydrogen and Carbon Monoxide  
Peterson Ridge, LLC**

Task Designation/Milestone	FY2002					2003
	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr4	Qtr 1
Main Effect Testing				◆		
Interferent Testing					★	
Sensor Fabrication			◆			
Outsource 2 <sup>nd</sup> Generation Fabrication			◆			
Demonstration Development Plan				◆		
Alpha Prototype Design and Assembly					◆	
Prototype and Reformer Test						◆
Prototype Redesign and Test						◆

FY2002 Begins October 1, 2001



= Critical Milestone



= Milestone

## **Design and Development of New Nanoengineering Glass-Ceramic Proton Conducting Membranes (GCPCMs) for High Performance H<sub>2</sub>-O<sub>2</sub> Proton Exchange Fuel Cells – Iowa State University**

An entirely new class of high-temperature, anhydrous, fast proton conducting (FPC) membranes will be designed and developed for use in new high-performance hydrogen–oxygen fuel cells. These new NanoEngineered glass-ceramic proton conducting membranes (GCPCMs) are expected to yield high proton conductivities,  $>10^{-1}(\Omega\text{cm})^{-1}$  between 100 and 300°C, excellent thermal stability up to 300°C, superior electrochemical and chemical stability, and zero fuel cross-over diffusion. These high-performance GCPCMs are expected to solve many if not all of the critical problems currently seen in the proton conducting membrane of choice Nafion<sup>TM</sup> used in polymer electrolyte membrane (PEM) fuel cells. GCPCMs are expected to yield higher conductivities, greater chemical, and electrochemical stabilities, higher temperature operation, and zero fuel cross-cover compared to Nafion<sup>TM</sup>.

In this project, FPC chalcogenide glasses already being developed in the Principal Investigator's (PIs) laboratory will be processed by well-known glass-ceramic processing routes to yield GCPCMs with controlled and optimized nanostructures. In a typical experiment, a hydrogen iodide- and hydrogen sulfide- doped boron trisulfide glass will be cast as a thin film, cooled to a nucleation temperature just below the softening point of the glass, held for a period of time to create nuclei of the FPC phase, and then heated to a growth temperature just above T<sub>g</sub> to crystallize the glass to a predetermined and optimized crystallite size and volume fraction of the FPC phase.

Once processed, the GCPCMs will be characterized. Their thermal, electrical, and physical properties will be determined, as will their atomic structures. Once optimized GCPCM electrolyte membranes have been prepared and characterized, these will be used to fabricate simple laboratory-scaled H<sub>2</sub>-O<sub>2</sub> fuel cells to characterize their fuel-cell performance.

### **Task 1: Synthesis of Proton Conducting Glasses**

GeS<sub>2</sub>-based glasses and polycrystals will be doped with H<sub>2</sub>S into the melt by a combination of gas bubbling and high-pressure reaction techniques. In a typical process for the former technique, a melt of ~ 3 grams of GeS<sub>2</sub> held in a chemically inert carbon crucible at a processing temperature of 500 to 800°C will be saturated with H<sub>2</sub>S by bubbling the gas into the melt using a ceramic tube lance placed just below the melt line. The processing conditions, time, temperature, and flow rate of H<sub>2</sub>S gas will be systematically examined to optimize the incorporation of H<sub>2</sub>S into the melt. In a typical process for the latter technique, a charge of GeS<sub>2</sub> will be placed in a vitreous carbon crucible and then loaded into a stainless steel reactor or into the reactor alone without the crucible and then pressurized with H<sub>2</sub>S with up ~ 100 PSI. The reactor and contents will then be heated between 600 and 900°C for varying lengths of time. The reactor will then be cooled to RT and the reacted materials characterized in Task 2.

Subtask 1.1: Synthesize glassy GeS<sub>2</sub>

Subtask 1.2: Perform H<sub>2</sub>S-bubbling experiments to dope glassy GeS<sub>2</sub> with H<sub>2</sub>S

Subtask 1.3: Perform high pressure sealed reactor experiments to dope glassy GeS<sub>2</sub> with H<sub>2</sub>S

Subtask 1.4: Develop optimized processing conditions to maximize concentration of protons in glassy GeS<sub>2</sub>



## **Task 2: Characterization of the Physical and Electrochemical Properties of Glass and Glass-Ceramic Proton Conducting Materials**

The physical properties of the glass and glass-ceramic materials produced in Task 1 above will be determined using a variety of techniques. DSC and DTA will be used to determine the glass transition, crystallization, and melting temperatures. Archimedes method will be used to determine the density of the glasses. The chemical durability in air and water will also be determined during the density measurements by using water as the immersion fluid.

The impedance of the glasses and glass-ceramics as a function of temperature and frequency will be measured to determine the proton conductivity using a Gamry impedance analyzer. Cyclic voltammetry will be used to determine the electrochemical properties of the glasses and glass ceramics, and where appropriate, high impedance electronic conductivity experiments will be performed to determine the electronic conductivity of the samples.

Subtask 2.1: DSC and DTA will be used to determine the glass transition, crystallization, and melting temperatures of the glasses, glass-ceramics and polycrystals

Subtask 2.2: Archimedes method will be used to determine the density of the glasses, glass-ceramics and polycrystals. The chemical durability in air and water will be determined at the same time by following the weight of these materials in air and water as a function of time.

Subtask 2.3: The ionic conductivity of the GCPCMs will be determined by using impedance spectroscopy as a function of temperature and frequency.

Subtask 2.4: The electrochemical behavior of the GCPCMs will be determined by using standard cyclic voltammetry methods on GCPCMs configured with platinum electrodes and cycling the electrolyte in voltage between oxidizing and reduction potentials.

## **Task 3: Characterization of the Structure of GCPCMs**

Structural characterization of the GCPCMs will be carried out using IR spectroscopy (examination of the -SH and contaminate -OH structures), Raman spectroscopy (examination of the germanium sulfide structures), x-ray diffraction (determination of the crystalline phases formed during glass ceraming), and by  $^1\text{H}$  MASS-NMR (detailed examination of the structure and formation of non-bridging sulphurs in the glass through the addition of  $\text{H}_2\text{S}$  to the glass). Collaboration with groups in Chemistry (x-ray crystallography) and Physics (NMR) to carry out many of these experiments is necessary.

Subtask 3.1: GCPCMs will be ground together with an excess of IR-grade KBr and pressed into a "KBr" pellet. IR spectroscopy will be used to characterize the relative concentration of -SH (thiol) and -OH (hydroxide) groups in the glass.

Subtask 3.2: Raman spectroscopy will be used to characterize the nature and relative concentration of the boron sulfide structures in the GCPCMs.

Subtask 3.3: x-ray diffraction will be used to determine the relative concentrations and structures of crystalline phases in the material

Subtask 3.4:  $^1\text{H}$  will be used to determine the short-range structures involving protons.

Subtask 3.5:  $^1\text{H}$  will be used to determine the proton conduction dynamics as a function of frequency and temperature and compared to similar measurements using impedance spectroscopy.

#### **Task 4: Glass-Ceraming of Proton Conducting Glasses**

Optimized  $x\text{H}_2\text{S} + (1-x)\text{GeS}_2$  glasses will be processed into glass-ceramic membranes by subjecting the glass to a glass-ceramic processing time-temperature profile. Given the fact that the membrane will operate in a very specific directional manner, that is the protons are expected to conduct across the thin direction of the film, it is important to optimize the underlying ceramic nanostructure and texture to this direction. The preferred texture is to have the microcrystal c-axes aligned in the direction of the preferred conduction.

Subtask 4.1: Proton-doped glassy  $\text{GeS}_2$  samples will be subjected to glass-ceraming heat treatments where the glass is heated to a nucleation temperature, held for a period of time, then heated to a slightly higher growth temperature to allow crystalline nuclei to grow and fully crystallize the glass.

Subtask 4.2: Preferred directional growth of the crystallites in the sample will be controlled by inducing nucleation on one side of the sample by quenching one side of the sample. Solidification microstructures will then be encouraged to grow across the thickness of the sample.

#### **Task 5: Characterization of the Microstructure of GCPCMs**

The crystalline microstructure of the GCPCMs prepared in Task 4 will be examined using a variety of techniques. Primarily, SEM and TEM techniques will be used on carefully sectioned and polished samples to examine the texture, microstructure, and crystallization morphology as a function of glass-ceraming processing conditions. Glass-ceraming conditions will be optimized to produce oriented nano-scaled crystallization morphologies perpendicular to the axis of the samples.

Subtask 5.1: SEM and EDS examination of the microstructures and compositions of GCPCMs as a function of glass-ceraming process conditions. Investigation of the relationship between glass-ceraming process conditions and GCPCMs microstructure.

Subtask 5.2: TEM examination of the microstructures and compositions of GCPCMs as a function of glass-ceraming process conditions. Investigation of the relationship between glass-ceraming process conditions and GCPCMs microstructure.

#### **Task 6: Fabrication of Fuel Cells based on GCPCMs**

If the proton conductivity and chemical durability's of the GCPCMs are sufficient, small laboratory scaled fuel cells will be constructed to characterize the efficacy of using GCPCMs in  $\text{H}_2\text{-O}_2$  fuel cells.

Subtask 6.1: Small laboratory-scaled fuel cells will be constructed from selected and optimized GCPCMs as prepared and characterized in the Tasks above.  $\text{H}_2$  will be used as the fuel and  $\text{O}_2$  will be used as the oxidizer. A variety of catalysis will be explored for both the cathode and anode sides of the cell. Pt will not likely be used due to the poisoning of Pt by sulfide materials. A variety of typical transition materials will be explored.

Subtask 6.2: Characterization of the fuel cell performance will be conducted by determining the current – voltage output from the cells as a function of cell conditions. The stability of the fuel – cell will be determined by measuring these outputs as a function of time.

**Design and Development of New NanoEngineering Glass-Ceramic Proton Conducting Membranes (GCPCMs) for High Performance H<sub>2</sub>-O<sub>2</sub> Proton Exchange fuel Cells**  
**Iowa State University**

Task Designator/Milestone	2002					2003
	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4	Qtr 1
<b>Task 1 Synthesis of Proton Conducting Glasses</b>						
Subtask 1.1 Synthesize glassy GeS <sub>2</sub>		◆				
Subtask 1.3 Perform high pressure reactions			◆			
Subtask 1.4 Optimizing processing conditions				★		
<b>Task 2 Characterization of the GCPCM</b>						
Subtask 2.1 DSC and DTA Characterization			◆			
Subtask 2.2. Density and chemical durability			◆			
Subtask 2.3 Ionic conductivity measurements				★		
Subtask 2.4 Electrochemical Characterization					◆	
<b>Task 3 Characterization of the Structure of GCPCMs</b>						
Subtask 3.1 IR Spectroscopy			◆			
Subtask 3.2 Raman spectroscopy			◆			
Subtask 3.3 <sup>1</sup> H NMR Spectroscopy				◆		
<b>Task 4 Glass-Ceraming of Proton Conducting Glasses</b>						
Subtask 4.1 Glass-ceraming heat treatments				◆		
Subtask 4.2 Directional solidification					◆	
<b>Task 5 Characterization of the Microstructure of GCPCMs</b>						
Subtask 5.1 SEM and EDS analysis of precursors					◆	
Subtask 5.2 SEM and TEM of solidified GCPCMs					◆	
<b>Task 6 Fabrication of Fuel Cells based on GCPCMs</b>						
Subtask 6.1 Construction of fuel cells					◆	◆
Subtask 6.2 Characterization of fuel cells						★

FY2002 Begins October 1, 2001



= Critical Milestone



= Milestone

## INTERNAL COMBUSTION ENGINES / TURBINES

### Internal Combustion Engines Research and Development – Sandia National Laboratories

Internal combustion engine cycles are fundamentally capable of greater than 50% efficiency. In addition, the power output characteristics of an auxiliary power unit (APU) for a hybrid vehicle are different than for conventional cars. By rethinking the problem from a blank sheet of paper a new approach has materialized.

The approach utilizes a free piston oscillating between two combustion chambers, and generating electricity directly from the oscillatory motion of the piston. Combustion occurs when a homogeneous fuel/air charge is compression heated to the point of reaction. In this way both rapid reaction rates, approaching constant volume combustion, and extremely lean mixture combustion, which essentially eliminates NO<sub>x</sub> formation, is realized. This appears to be the combustion approach that can achieve both high efficiency and low emissions, but still retain highly developed reciprocating engine technology and fuel flexibility required to transition to a hydrogen energy carrier society.

Since the fuel/air mixture, which is delivered premixed to the cylinder, is ignited by compression heating, the piston position at the time of combustion is determined by compression ratio and initial temperature. The free piston configuration provides a method for controlling the compression ratio electronically, thus allowing continuous optimization of performance and fuel flexibility.

The first goal of Sandia's research is to demonstrate the efficiency and emissions performance of a 30 kW generator in a research environment. Following this accomplishment will be refinement of the research unit into a fieldable unit for demonstration, coupled with a wind generator and used for generation when wind power is down.

To date the combustion characteristics of homogeneous charge compression ignition with a free piston have been demonstrated. Also, the design of the linear alternator, which converts the piston oscillation to electrical energy, is finished. Three alternators from Magnequench International have been fabricated, with two of these devices at Sandia. The Sandia design alternator has experienced assembly tolerance problems and is being resized for assembly. The two stroke cycle design parameters have been decided based on CFD (KIVA 3V) code calculations. The tasks remaining are the experimental characterization of the linear alternator, testing of the two-stroke cycle inlet/exhaust process, development of control system algorithms and hardware, diagnostics and startup processes.

For FY 2002, if funding and manpower permits, the following tasks will be accomplished:

**Task 1:** Redesign the Sandia alternator for greater clearance between the coils and stator sections, allowing for extra insulation of the coil from the stator.

**Task 2: (Key milestone)** Test the Magnequench design alternator. The alternator by itself will be driven through a 6-inch stroke at 35 Hz by the modified Caterpillar 3304 engine. Measure the electrical output of the alternator and the loads on the stator assembly to determine conversion efficiency. Produce a summary document of the Magnequench alternator performance.

**Task 3:** Assemble the Sandia alternator, and test on the Caterpillar engine tester.

**Task 4:** Fabricate the two stroke cycle experiment based on uniflow scavenging

**Internal Combustion Engines Research and Development  
Sandia National Laboratory**

Task Designation/Milestone		FY2002					2003
		Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4	Qtr 1
Task 1. Redesign Sandia Alternator				◆			
Task 2. Test Magnequench Alternator			★				
Task 3. Assemble and test Sandia Alternator					◆		
Task 4. Fabricate Uniflow scavengin experiment						◆	

FY2002 Begins October 1, 2001

★ = Critical Milestone

◆ = Milestone

## **Reduced Turbine Emissions Using Hydrogen-Enriched Fuels – Sandia National Laboratories**

The goal of this program is the development of advanced combustion capabilities for gaseous hydrogen and hydrogen-blended hydrocarbon fuels in gas turbine applications. Driving this interest are several current needs. One need is the cost-effective utilization of alternative fuels with a wide range of heating values. For example, low and medium heating value fuels containing hydrogen are often produced as a by-product in Coal-Gasification Combined Cycle installations. These product gases could provide a significant source of cost-effective fuels for gas turbines. A second need is related to the recognition that ultra-lean premixed combustion is an effective approach to NO<sub>x</sub> emissions reduction from gas turbine engines. Hydrogen blended with traditional hydrocarbon fuels significantly improves flame stability during lean combustion and allows stable combustion at the low temperatures needed to minimize NO<sub>x</sub> production. A longer-term need is the desire to eliminate UHC and CO<sub>2</sub> emissions entirely. The use of hydrogen-blended fuels provides both a solution to the immediate need for NO<sub>x</sub> reduction, and also provides a transition strategy to a carbon free energy system in the future.

Changes in fuel composition, particularly the addition of hydrogen to hydrocarbon fuels, affect both the chemical and physical processes occurring in flames. These changes affect flame stability, combustor acoustics, pollutant emissions, combustor efficiency and other important quantities. Few of these issues are clearly understood. This program will investigate issues surrounding hydrogen-enriched hydrocarbon fuel use and will include studies of chemical kinetics, combustion fluid dynamics, laminar and turbulent flame structure to better define and understand these issues.

### **Task 1: Lean-Premixed Swirl Burner**

This burner, developed in FY2001 in collaboration with NETL, is a lean premixed swirl-stabilized burner representative of power-generation gas turbine combustors. During FY2002, a range of hydrogen/natural gas blends will be studied to quantify the effect of hydrogen addition on lean flame stability and on the extension of the lean flammability limits to minimize NO<sub>x</sub> production. Detailed mapping of the velocity, temperature and species concentrations fields will be carried out to provide the basis for understanding the effects of hydrogen addition on combustion dynamics. Techniques will be identified for optimal utilization of hydrogen-blended fuels in practical gas turbines combustors. A Computational Fluid Dynamics (CFD) model will be developed in parallel with the experimental effort, with the experimental data providing the basis for model validation.

### **Task 2: Hydrogen Burner Development**

This burner, developed during FY2001 with the NASA Glenn Research Center, focuses on the use of hydrogen as an alternative aircraft fuel. A prototype, atmospheric-pressure burner has been fabricated and installed at Sandia. Next year the burner operation will be characterized over a range of operating conditions with an emphasis on quantifying fuel/air mixing and flame stability. Based on these measurements improvements will be identified and implemented. Detailed measurements of velocity, temperature and gas species will be obtained to characterize flame stability and pollutant formation during hydrogen combustion.

### **Task 3: Economic Analysis of Hydrogen-Blended Fuels**

Efforts will continue on an economic analysis to establish the benefits of hydrogen addition to the stationary gas turbine community. This task is being carried out under subcontract by Energetics Inc. The cost analysis will include greenhouse and CO<sub>2</sub> emissions reduction and NO<sub>x</sub> and air toxics reduction. Base case cost and emissions levels for current mid-sized turbines will be established, potential system

designs will be identified and comparisons with base case values will be made to determine beneficial scenarios.

#### **Task 4: Industrial Collaborations**

In collaboration with and at the request of General Electric (H. Mongia) and University of Cincinnati (E. Gutmark) a test program that is specific to a General Electric multi-swirl fuel injector (TARS configuration) will be developed. Specific tasking areas will be identified and tests initiated. Sandia will derive requirements for the scaling of atmospheric pressure testing to practical gas turbine operating conditions. Test results will be evaluated in relationship to specific areas of interest to the TARS geometry. Experimental results will be used to validate LES models, which are of direct current interest to the General Electric modeling program. Fundamental modeling issues that have direct applicability to the TARS geometry will be addressed.

#### **Task 5: International Collaborations**

Participation in the IEA Hydrogen Annex: The objective of this program is the development of an international effort to address fundamental and applied aspects of hydrogen-enriched hydrocarbon fuels for ultra-lean premixed gas turbine combustion. During FY2001 a work plan was developed and important task areas were identified. In particular, the development of the next generation modeling and predictive capabilities for turbine design with hydrogen enrichment was identified as a flagship task. During FY2002 program areas will be parsed off and funds from international sources will be solicited. Sandia will continue to work with the IEA to develop a robust plan for the next generation of models.

**Reduced Turbine Emissions Using Hydrogen-Enriched Fuels**  
**Sandia National Laboratories**

Task Designation/Milestone	FY2002					2003
	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4	Qtr 1
<b>Task 1: Lean-Premixed Swirl Burner</b>						
Characterize burner operation			◆			
Quantify effect of hydrogen addition				★		
Complete OH PLIF measurements						◆
Complete velocity measurements						◆
<b>Task 2: Hydrogen Burner</b>						
Characterize burner operation		◆				
Evaluate fuel/air mixing and implement improvements			★			
Complete OH PLIF measurements				◆		
Complete velocity measurements					◆	
<b>Task 3: Economic Analysis</b>						
Establish base case cost and emissions levels	◆					
Compare designs with base case			◆			
Determine beneficial scenarios				◆		
<b>Task 4: Industrial Collaborations</b>						
Develop experimental test matrix			◆			
Derive pressure scaling laws				◆		
Initiate testing					◆	
<b>Task 5: International Collaborations</b>						
Parse off program areas and solicit funding			◆			
Develop plan for next generation CFD models					◆	

FY2002 Begins October 1, 2001

★ = Critical Milestone

◆ = Milestone



### **Hydrogen/Natural Gas Blends – NRG Technologies**

*This project is currently being negotiated.*

## **HYDROGEN SAFETY**

### **Interfacial Stability of Thin Film Hydrogen Sensors – National Renewable Energy Laboratory**

The goal of this project is to develop safe, low cost, lightweight hydrogen sensors that can be used as safety sensors where hydrogen is used, stored, or transported. These sensors must be inexpensive enough to use several of them on a hydrogen powered vehicle, and they must be sensitive and fast enough to provide early leak detection so that action can be taken before the explosive limit in air is reached. NREL's efforts are focused on developing a better understanding of the service lifetime and performance issues that will enable the thin film hydrogen sensors to be commercialized. They will continue real time as well as accelerated testing of sensor films for determining the durability and reliability of these sensors. NREL will also test the sensor films under a range of temperatures (-40 °C to 40 °C), relative humidity (0 to 100%), and various concentrations of environmental pollutants.

The project objective for FY 2002 is to demonstrate sensor configurations, meeting the project goal, that have service lifetimes of 6 months or greater. A further goal is to work on active layer modifications that can simplify component engineering activities and accelerate commercialization of these sensors.

The technical challenges remaining are related to performance issues of the sensor construction under varying environmental conditions that are anticipated in the field of use for the sensors. Specifically, these relate to performance characteristics under wide ranges of ambient temperature and relative humidity, as well as stress factors, such as doses of pollutants from internal combustion engine exhaust or other species emanating from our industrial society. Also, NREL needs to determine just how long these sensors will last when stored on the shelf, placed in service, and cycled repetitively in hydrogen and contaminated gas streams. This will require real-time as well as accelerated testing. Finally, NREL has the opportunity to significantly reduce the product engineering effort in the future by making some modifications to the protective film layers. This will reduce the cost of the whole sensor and control package.

#### **Task 1: Sensor Service Lifetime**

NREL will continue to operate sensor elements currently in environmental tests in order to explore the service lifetime issue. In addition, they will construct and test new sensors with pollutants and cycle the sensors with hydrogen to determine if acceleration can be achieved in the loss of performance of the sensors.

#### **Task 2: Study the effects of variations in temperature and humidity**

NREL expects that the diffusion of hydrogen into the thin film stacks of the optical sensor will slow as temperature is reduced. Consequently, they expect response times of the sensor to increase substantially as temperature is decreased. This effect needs to be measured in order to determine the temperature range of the sensor for effective performance as a safety sensor. Additionally, NREL expects that the response or the lifetime of the sensor may be affected by changes in relative humidity. Therefore, the effects of variation in humidity of the sensor environment need to be explored.

<b>Interfacial Stability of Thin Film Hydrogen Sensors</b> <b>National Renewable Energy Laboratory</b>						
Task Designation/Milestone		FY2002				2003
	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4	Qtr 1
<b>Task 1: Sensor Service Lifetime</b>						
Report progress in determining sensor lifetimes					★	
<b>Task 2: Study the effects of variations in temperature and humidity</b>						
Modify the test chamber for conducting experiments at controlled temperatures and humidity			◆			
FY2002 Begins October 1, 2001      ★ = Critical Milestone      ◆ = Milestone						

## **Integrated Micro-Machined Hydrogen Gas Sensors – Advanced Technology Materials, Inc.**

The DOE Hydrogen R&D program has been charged with developing the technologies necessary to safely produce, store, transport and utilize hydrogen as an energy carrier; illustrating the energy and environmental benefits of hydrogen as an energy carrier to the public; and initiating the transition strategy which can bring these technologies to the marketplace.\* An underlying need in each of these areas is the ability to detect and quantify the amount of gaseous hydrogen gas present. This is critical not only for health, safety and public perception, but also for the development of highly efficient hydrogen processes. Economical hydrogen gas sensors that can quickly and reliably detect hydrogen over a wide range of conditions and concentrations are not currently available, and must be developed to facilitate the transition to a hydrogen based energy economy.

ATMI's approach to satisfy these required hydrogen detection needs is the development of MEMS (Micro-Electro-Mechanic System) based, solid-state, hydrogen gas sensors. These sensors couple novel thin films as the active layer on device structures known as micro-hotplates. Such hydrogen gas sensors have several unique advantages in terms of speed, selectivity sensitivity, stability, power consumption as well as amenability to large scale manufacture.

To date, ATMI has successfully designed and fabricated Integrated Micro-Machined hydrogen gas sensors, and tested the hydrogen response of these devices. These sensors have demonstrated exceptional responsivity, with measured changes in resistance of >120% for 0.25 % H<sub>2</sub> concentrations and response times <0.5 sec. Initial testing also demonstrated the ability of the sensor to respond to hydrogen in air with high humidity, as well as in inert (dry nitrogen) conditions.

Based on the success of these initial investigations, ATMI is continuing the development and evaluation of Micro-Machined Hydrogen Gas Sensors. Although they have demonstrated the feasibility of coupling the micro-hotplate with novel thin films for hydrogen sensing, there remain a number of issues to be addressed. These include microhotplate platform optimization, investigation of the resiliency of these sensors to potential contaminants and cross interference, and demonstration long-term operational stability. These issues will be addressed in FY2002, as described in the following section.

### **Tasks:**

In order to further the development of these sensors, the following tasks have been identified: 1) Sensor Design and Fabrication optimization 2) Testing of potential contaminants and cross interferences 3) Long Term Behavior Investigation, and are described below.

### **Task 1: Sensor Design and Fabrication Optimization**

To date, ATMI has produced micro-hotplate based gas sensors, using palladium coated metal hydrides as the hydrogen selective active layer. Sensor device processing consists of several steps: CAD design, CMOS fabrication, active layer functionalization, and packaging. In this task, they will continue to build on this base, and concentrate on the optimization of the MEMS device platform as well as device processing. In the design optimization, we will minimize the device size and power requirements, while process optimization will concentrate on maximizing device yield and reproducibility. This task will be an iterative process, incorporating feedback from the sensor response testing results of the other tasks. Similarly, the results of this task will have a direct impact on the response testing tasks. For example, improvements in the thin film processing of the sensor are expected to influence both short and long term sensor performance. Thus parallel execution of this task in conjunction with the testing tasks is a direct result of inter-relation of processing and performance.

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\* FY2001 Annual Operating Plan: Hydrogen Program, December 2000

## Task 2: Testing of Potential Contaminants and Cross Interference

The sensors produced to date have been successfully tested in a fully automated gas-sensing manifold, specifically designed and constructed for this project. This manifold will be expanded in the FY2002 in order to examine the effect of potential contaminant gases on sensor performance. In addition, the effort to examine cross sensitivities and contaminant gases, as well as temperature effects, will be extended through collaboration with outside industrial partners. Potential contaminant gases of interest will include: carbon monoxide, sulfurous compounds, and hydrocarbons such as benzenes, aldehydes and ketones.

## Task 3: Investigation of Long Term Operational Stability

The long term stability and behavior of the sensor is an important consideration for nearly all potential applications. In FY2002, ATMI will continue these investigations of the long-term performance of these sensors, and determine what, if any, change in performance occurs as a function of time. They will perform experiments to develop an understanding of any potential drift mechanisms observed in these devices and the effect operating conditions have on these mechanisms. This task will tie in closely with the tasks above, and the ultimate goal of this will be to demonstrate a sensor device with an extrapolated lifetime of 3 years.

Integrated Micro-Machined Hydrogen Gas Sensors Advanced Technology Materials, Inc.						
Task Designation/Milestone		FY2002				2003
		Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4
<b>Design and Fabrication Optimization</b>						
Submit New MEMS Design for Fabrication		◆				
Optimize Fabrication Processes			◆			
Choose Best MEMS Design				◆		
<b>Testing of Potential Contaminants and Cross Interferences</b>						
Complete ATMI Interference Tests				◆		
Complete Cross Sensitivity Testing at Collaborator					◆	
<b>Investigation of Long Term Operation Stability</b>						
Construct long term testing manifold		◆				
Develop and validate lifetime extrapolation method			◆			
Demonstration of Sensor with 3 Yr extrapolated lifetime						★
FY2002 Begins October 1, 2001      ★ = Critical Milestone      ◆ = Milestone						

## **Codes and Standards Analysis – University of Miami**

### **Technical Summary of Project**

**Task A** is composed of three parts:

A-2 - Hydrogen plume ignition tests

A-3 - Computational Fluid Dynamics (CFD) modeling of 2 accident scenarios

A-4 - Hydrogen bus leak ignition tests

Part A-2: Hydrogen burns in air at concentrations between 4.1% and 75%. Whenever hydrogen leaks into air a burnable mixture of hydrogen and air is formed. The total volume of that burnable cloud determines the severity of an accidental ignition of the cloud. The volume of the burnable cloud is a function of leakage rate and gas motion. Computer models of leakage at the CaFCP building have shown the volume of burnable hydrogen air mixtures that can be expected for high probability leaks. This part would experimentally determine the severity (over pressure) caused by ignition of these clouds. The work would measure the effects of ignition of the clouds both inside and outside a warehouse of similar volume to that in Sacramento.

Part A-3: This part is the CFD modeling of two accident scenarios for the California Fuel Cell Partnership (CaFCP) building. The computer model has been created during the first year's work. New accident scenarios typically include writing additional software to work in conjunction with the main CFD model. Modeling a given accident scenario is done to give additional insight into a given safety procedure or vehicle location restriction.

Part A-4: The ignition of hydrogen air mixtures trapped under vehicles creates a rapid pressure increase under the vehicle. This is called overpressure, referring to the increase above atmospheric pressure. These have previously been measured for hydrogen air mixtures trapped in a bus wheel well and were found to be less than 0.2 PSI for leakage rates up to 5 SCFM of pure hydrogen. The values are substantially lower than the theoretical stoichiometric predictions because the constraints of fluid dynamics caused most of the hydrogen air mixture to be either too rich or too lean to burn rapidly. This part is to show the possible over pressure created by ignition of hydrogen air mixtures trapped under vehicles. A full-scale model of the front half of a bus has been previously constructed. It will be used to experimentally determine how large an over pressure can be created by hydrogen leaking under a vehicle.

**Task B** is comprised of one part:

B-1 - Develop apparatus for determining sensor location

Part B-1: This part will develop an apparatus and procedure that creates helium bubbles of the proper size and density to approximate the path of leaking hydrogen. It is felt that this will be possible because even though hydrogen and helium differ in density, they still transverse similar paths when released in an air environment. The buoyancy forces that dominate the flow are similar, though helium is twice the density of hydrogen, because both densities are so much lower than the density of air. The size and degree to which released soap bubbles are connected to one another can be controlled with the geometry of the holes creating the bubbles. Results of Task B will be used to determine if it is possible to develop a quick method to utilize helium bubbles to show the expected pathway of leaking hydrogen. It may be possible to devise a simple, quick, procedure to assist in the optimal location of hydrogen sensors.

**Task C** is comprised of two parts:

C-3 - ICC Code Submittal Meeting

## C-4 - CFD modeling of 2 accident scenarios for Spring ICC Hearings

Part C-3: The International Code Council (ICC) Ad Hoc Committee is comprised of 12 members. Three members are industrial representatives. One of those three is Dr. Swain. Working group 1 (WG1) is writing the proposed codes for Residential Garages and WG4 is writing the proposed codes for Portable FC Appliances. Both groups need data to determine whether single or double 5/8" Fire code gypsum board should be required for construction of enclosures for devices using hydrogen. The projections made from last year small-scale tests indicated single 5/8" should provide the necessary hydrogen flame impingement protection. This part involves the preparation, review of the proposed codes, and travel for submittal in November.

Part C-4: This part involves the modeling or experimental analysis of two accident scenarios in preparation for the spring ICC hearings for acceptance. The hearings will be attended to present the results in support of the proposed codes.

**Tie-in of Future Plans**

As stated in the Future Plans from the Annual Review, the project is continuing to determine experimentally and through the use of CFD modeling what restrictions Codes and Standards should place on the buildings which house vehicles and appliances using hydrogen. Additionally, Task B was designed to aid in the placement of hydrogen sensors within a building. Sensor placement plays a strong role in determining how quickly the sensor can detect hydrogen.

Codes and Standards Analysis University of Miami						
Task Designation/Milestone	FY2002					2003
	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4	Qtr 1
A1 – CFD modeling of 2 accident scenarios		◆				
A2 – Hydrogen plume ignition tests		◆				
A3 – CFD modeling of 2 accident scenarios			◆			
A4 – Hydrogen bus leak ignition tests				★		
A5 – Final Writeup					◆	
B1 – Develop apparatus for determining sensor location				★		
B2 – Final Writeup					◆	
C1 – Large scale gypsum board tests	◆					
C2 – ICC Code Review in Cincinnati		◆				
C3 – ICC Code Submittal Meeting		★				
C4 – CFD modeling or experimental analysis of 2 accident scenarios for Spring ICC Hearings				◆		
C5 – Final Writeup					◆	

FY2002 Begins October 1, 2001      ★ = Critical Milestone      ◆ = Milestone

## **High Efficiency Steam Electrolyzer – Lawrence Livermore National Laboratory**

The objective of this Research & Development project is to develop a novel, low cost and highly efficient high temperature steam electrolyzer for distributed hydrogen production. Although water or steam electrolysis is well known to be one of the cleanest ways to produce hydrogen, its widespread utilization is hindered by high operational cost due to high electricity consumption. LLNL's approach to decrease the electrical power input requirements in electrolysis is to use natural gas as an anode depolarizer. This approach essentially replaces one unit of electricity by one equivalent energy unit of natural gas at one-fourth the cost. There are two possible modes of operation. In the total oxidation mode, i.e. when methane is just used to reduce the electrochemical potential difference between the two sides of the electrolyzer membrane, the system does not require any gas separation and has the potential to produce pure hydrogen at high pressures. In the partial oxidation mode, methane is converted to hydrogen and carbon monoxide, which is subsequently converted to hydrogen via the water gas shift reaction. LLNL chose to focus our current efforts on the development of a system operating in the total oxidation mode because of its simplicity. Using appropriate system design, it is possible to electrochemically compress hydrogen in-situ, thus eliminating the need for an expensive hydrogen compressor. Although the present approach still involves fossil fuels, due to the significantly higher efficiency, the carbon emissions will be reduced. Furthermore, off-board hydrogen production (as opposed to on vehicle reforming of hydrocarbon) will enable the sequestration of CO<sub>2</sub>, thus eliminating greenhouse gas emissions. The use of fossil fuels is an evolutionary step for the transitional phase to an economy that is based on purely renewable energy.

From FY99 through 01, LLNL has developed electrolyzer materials as well as small proof-of-concept stacks. In FY02, the project enters the second phase, i.e. the demonstration of a scale-up electrolyzer system. The goal is to demonstrate a semi-integrated 1 kW prototype in 2003 and a fully integrated 5 kW prototype in 2005. This work will be done in collaboration with American Fuel Cells, LLNL's industrial partner.

### **Project Tasks**

#### **Task 1: Continue materials development and optimization**

##### Subtask 1.1: Optimize sealant

LLNL has developed a metal-to-ceramic brazing approach as sealant for the electrolyzer tubes. Due to issues with thermal expansion mismatch and surfaces wetting, their current seals have a maximum working pressure of 80 psi. They propose to improve the seal by developing interfacial layers that will improve this joint.

##### Subtask 1.2: Improve tube electrochemical performance

The electrochemical performance of the current electrolyzer tube is, at best, 30% of that of single flat disks. The difference in performance is most likely due to the difference in microstructure between the tube and the disks. For this task, LLNL will identify the origin of the low tube performance and will develop the right tube microstructure to improve tube performance.

#### **Task 2: Demonstrate long-term stability**

Long-term stability is a critical factor for commercial application. LLNL will first determine stability of single cells for 100 hours of operation. The possible degradation of each of the electrode will be identified using three-electrode measurement technique. The long-term stability will be improved by altering the electrode microstructure.



### Task 3: Key milestone: Scale up fabrication process

None of the electrolyzer components is currently commercially available. The objective of this task is to develop and to demonstrate fabrication techniques that are suitable for low cost mass-production. This task is a cornerstone for future scale-up and commercialization.

#### Subtask 3.1: Demonstrate 12" green tube fabrication

LLNL will develop a process to fabricate 12" tubes using injection molding or extrusion techniques.

#### Subtask 3.2: Determine tube processing conditions

The processing conditions for various steps, including binder burnout, pre-sintering, thin film coatings, full sintering, will be determined in order to obtain high quality tubes.

### Task 4: Stack engineering

In this task, NREL will explore various alternative stack designs. The stack design is currently limited by the maximum length of the electrolyzer tube that they can fabricate (6 inches). By developing 12" tubes, other stack designs can be considered. NREL will develop computer models to explore the trade-offs associated with various designs.

### Task 5: Start fabrication of 1 kW stack prototypes

In order to demonstrate a 1 kW stack in FY03, NREL needs to start the scale-up effort in FY02. In this task, they will put together 12" tubes in various configurations to evaluate the stack designs developed in task 4. This effort will enable early identification and thus early resolution of potential issues in the scale-up.

High Efficiency Steam Electrolyzer Lawrence Livermore National Laboratory						
Task Designation/Milestone		FY2002				2003
	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4	Qtr 1
Demonstrate 200 W stack		◆				
Continue materials development and optimization						
Optimize sealant			◆			
Improve tube electrochemical performance			◆			
Demonstrate long-term stability				◆		
Scale-up fabrication process						
Demonstrate 12" green tube fabrication				★		
Determine tube processing conditions					◆	
Stack engineering						◆
Start fabrication of 1 kW stack prototypes						◆

FY2002 Begins October 1, 2001      ★ = Critical Milestone      ◆ = Milestone

### 3.2 Technology Validation

This section describes the projects that are being considered as key hydrogen implementation components. They include projects pertaining to renewable hydrogen systems, projects that will lead to the development of a hydrogen infrastructure, and projects that will lead to the development of hydrogen in remote areas. Technology Validation Tasks are listed in Table 3.5.

Table 3.5 Technology Validation		
Goal: Support industry in the development and demonstration of hydrogen systems in the utility and transportation sectors		
Category	Project	Researchers
<i>Renewable Hydrogen Systems</i>	Engineering Scale Up of Renewable Hydrogen Production by Catalytic Steam Reforming of Peanut Shells Pyrolysis Products	National Renewable Energy Laboratory
	Hydrogen from Biomass for Use in Urban Transportation	Clark Atlanta University
	Hydrogen Production Through Electrolysis	Proton Energy Systems
	Renewable Hydrogen System Integration and Performance Modeling	Desert Research Institute
	Hydrogen-Based Utility Energy Storage System	SRT Group
<i>Hydrogen Infrastructure</i>	Filling up With Hydrogen 2000	Stuart Energy Systems
	Light, Medium Duty Fleet	NRG Technologies
	Hydrogen Commercialization for the 21 <sup>st</sup> Century	SunLine Services Group
	Hydrogen and Fuel Cell Vehicle Evaluation	National Renewable Energy Laboratory
	Hydrogen Reformer, Fuel Cell Power Plant and Vehicle Refueling System	Air Products and Chemicals, Inc.
	Hydrogen Composite Tank Program	Quantum
	Insulated Pressure Vessels for Vehicular Hydrogen Storage	Lawrence Livermore National Laboratory
	Mine Locomotive and Loader Projects	Sandia National Laboratories
<i>Distributed Power</i>	Power Parks System Simulation Project	Sandia National Laboratories

## RENEWABLE HYDROGEN SYSTEMS

### **Engineering Scale Up of Renewable Hydrogen Production by Catalytic Steam Reforming of Peanut Shells Pyrolysis Products – National Renewable Energy Laboratory**

The goal of this project is the production of renewable hydrogen from agricultural residues, in the near-term time frame (~three years) and at a comparable cost to existing methane reforming technologies. The hydrogen produced will be blended with CNG and used to power a bus in Albany, GA.

NREL's strategy is to produce hydrogen from biomass pyrolysis oils in conjunction with high value co-products. Activated carbon can be made from agricultural residues in a two-stage process: (1) slow pyrolysis of biomass to produce charcoal, and (2) high temperature processing to form activated carbon. The vapor by-products from the first step can be steam reformed into hydrogen. NREL has developed the technology for bio-oil to hydrogen via catalytic steam reforming and shift conversion. The process has been demonstrated at the bench scale and Phase 1 testing of the reformer began in FY2001. A preliminary economic analysis of the base case process assumes utilization of all of the pyrolysis vapors (225 kg/hr) at the current scale of the Scientific Carbons Inc. process. For an annual hydrogen production rate of 4.4 million Nm<sup>3</sup>, the selling price of hydrogen is estimated to be \$9.50/GJ.

Project objectives for FY 2002 include:

- Scale up catalytic steam reforming process parameters as derived from the bench scale experimentation carried out at NREL to develop the process concept.
- Determine gas composition over the catalyst life cycle and compare to the purity requirements needed for the shift reactors and pressure swing adsorption unit. This will be performed at NREL using the Thermochemical Users Facility (TCUF). NREL's available analytical capabilities of TCUF will allow the process gas stream to be characterized and optimized for the subsequent operation at the Scientific Carbons plant in Georgia.
- Build and test a slipstream, two-stage, shift reactor and design a pressure swing adsorption unit to work with the system when it is operated in FY2003 in Georgia to produce hydrogen to run a bus.
- Participate in the Phase 2 testing work that will occur in Georgia at the Scientific Carbons site.
- Support the partnership development that will be necessary for the bus demonstration.
- Identify other biomass resources in the region that could be used to produce hydrogen in conjunction with the Scientific Carbons process or by other integrated biomaterial-processing technologies.

#### **Task 1: Process parameter scale up optimization and detailed product analysis to determine impact on the design and performance of downstream operations**

After successful shakedown of the reactor at NREL in FY2001, the NREL staff will continue to run the reactor in the first part of FY2002 to determine the optimum process parameters. Since the same level of process control and online analysis capability will not be available in Georgia, this information will be of value for the tests in Georgia later in the year. Since the reformer will not be needed in Blakely until the spring, this will not impact the scheduled demonstration in Georgia. NREL staff will perform detailed analysis of the product gases over the life cycle of the catalyst. Of particular concern are breakthrough products, such as hydrocarbons, that may be present in the product gases as catalyst activity decreases with time on stream. These products may physically or chemically diminish the performance of the shift reactors or the pressure swing adsorption units that will be needed to process the gas for use in transportation. This work will establish the need for guard beds and provide information to begin detailed discussions with the catalyst industry about the cost of performing these unit operations.

## Task 2: Gas Conditioning - design and testing of a slipstream shift reactor system and analysis of gas separation by pressure swing adsorption and membranes

A slipstream shift reactor (~10% or 1 kg/hour) will be built and monitored for performance as a function of time on stream. This adaptation will be straightforward and will provide the experience so that the team in Blakely can learn the proper management of this system and do the design for Phase 3. Test parameters will include catalyst activation and performance as a function of steam/hydrogen and CO/CO<sub>2</sub> ratios.

The process flow sheet has included pressure swing adsorption, but a detailed feasibility study needs to be done to determine the design and cost of the system once the actual gas composition is determined in Task 1. Given the scale of the demonstration, membrane technologies should be evaluated and compared for gas conditioning.

### Engineering Scale Up of Renewable Hydrogen Production by Catalytic Steam Reforming of Peanut Shells Pyrolysis Products National Renewable Energy Laboratory

Task Designation/Milestone	FY2002					2003
	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4	Qtr 1
<b>Task 1. Process parameter scale up optimization and detailed product analysis to determine impact on the design and performance of downstream operations</b>						
Determine optimum process parameter levels and document the resulting gas composition as a function of catalyst life cycle			★			
<b>Task 2. Gas Conditioning: design and testing of a slipstream shift reactor system and analysis of gas separation by pressure swing adsorption and membranes</b>						
Recommend design and implementation plan for the shift and separation steps for the Phase 3 demonstration in Georgia in 2003					◆	

FY2002 Begins October 1, 2001



★ = Critical Milestone



◆ = Milestone

## **Hydrogen from Biomass for Use in Urban Transportation – Clark Atlanta University**

Economic development and environmental improvement can be approached in an integrated fashion using an industrial ecology model that focuses on the energy and material links between industries and the community. The southeastern U. S. is an ideal place to develop such a model in a systemic way based on new uses for agriculture and renewable environmental and energy technologies. Agriculture is Georgia's largest industry and contributes over \$46 billion to the state's annual economic output. One in six Georgians work in an agriculture-related sector and Georgia ranks as the number one state in the U.S. in peanut production; producing about 45 % of all peanut grown in the U. S. Georgia farmers grow about 1.5 billion pounds of peanut in 79 counties. The 1998 production of peanut in Georgia was about 1.54 billion pounds (768,500 tons) which was 15 % more than that of 1997. Disposal of the large quantity of peanut shells is a significant environmental challenge. Peanut shells have therefore been targeted as the biomass feedstock for conversion to hydrogen for urban transportation.

Biomass can be converted to hydrogen by two distinct strategies: 1) gasification followed by shift conversion, and 2) fast pyrolysis followed by catalytic steam reforming and shift conversion of specific fractions. The National Renewable Energy Laboratory (NREL) technology is based on the latter approach and has the potential to be cost competitive with current commercial processes for hydrogen production. Bio-oil is easily transportable so the steam-reforming step can be carried out at a different location, close to the infrastructure for hydrogen use or distribution. The bio-oil produced from fast pyrolysis of biomass contains about 75-85 wt% organics and 15-25% water. The organics are generally a mixture of aldehydes, alcohols and acids derived from the carbohydrate fraction of biomass and phenolics from lignin. Fast pyrolysis produces two bio-oil fractions: a monomer-rich aqueous fraction (containing typically 20 wt% organics) and a hydrophobic fraction composed mainly of oligomers derived from lignin. Steam reforming can be conducted with the entire bio-oil or with fractions of the oil to yield hydrogen. The potential for the production and recovery of higher value co-products from the bio-oil that could significantly impact the economics of the entire process is a major advantage.

The economics of the NREL approach has been assessed with an adhesive coproduct and the selling price of hydrogen was determined to be in the range of \$6-8/MBTU. Phase 1 concentrated on the engineering R&D including the design, construction and testing of the fluidized-bed catalytic steam reformer system. Phase 2 will focus on integrating the reformer to a pilot-scale pyrolysis unit at Scientific Carbons Inc., a small company in Southwest Georgia that produces activated carbon by pyrolysis of densified peanut shells. The study will focus on the long term catalyst testing of the reformer with the pyrolysis by-product vapors, modeling of the feedstock supply economics and depolymerization strategies, coproducts development and experiments, hydrogen storage and utilization, and partnership building and outreach activities.

### **Task 1: Feed Supply, Process Economics and Deployment**

The ultimate impact of the biomass-to-hydrogen process will depend on the overall economics. Feedstock issues such as supply, cost and logistics will be a major factor in cost-effectiveness of the process. Task 1 will continue with the process and economic studies with particular emphasis on the co-product strategies of adhesives, hydrogen and activated carbon for municipal wastewater treatment. Other emphasis will be on the liquid-liquid extraction studies and physical property estimations.

*Milestones:* Development of models and solutions-June 2002; Solubility and physical property measurements-Sept. 2002; Process design and economics of process flow sheets-Dec. 2002.

### **Task 2: Reactor Modifications and Shake Down**

The initial shakedown of the reformer in Phase 1 is ongoing at NREL's Thermochemical Users Facility at Golden, CO. In Phase 2, a pilot scale pyrolysis unit will be designed, constructed, tested and

integrated/interfaced with the reformer at Scientific Carbons Inc. New control systems will be added to improve process control for the long duration runs that will be performed in Task 3. This is the major and most expensive task.

*Milestone:* Design and construction of the pilot-scale pyrolysis unit-March 2001; Shipping and interfacing of the reformer-June 2002; Shakedown of the integrated system-August 2002.

### **Task 3: Long-Duration Testing at Scientific Carbons, Inc.**

The combined pyrolysis-reformer system will be run from 100-200 hours. Catalyst activity will be monitored throughout the run. Feed rate will be varied as well as pyrolysis reactor severity.

*Milestone:* Complete 100-200 hours of operation at Scientific Carbons-September 2002

### **Task 4: Preparation for Hydrogen Storage and Utilization**

Past approaches to the storage of hydrogen in mixtures with compressed natural gas will be reviewed and calculation of mixture limits will be made. Other storage options will be explored that will meet the needs of the planned demonstration. Model system testing will be performed. In preparation for hydrogen utilization, Phase 2 will include working with community partners to define the transportation fleet applications. The design of a storage system will be done.

*Milestone:* Complete design of storage and utilization system-September 2002

### **Task 5: Environmental and Technical Evaluation**

This task will design, acquire, and prepare the necessary analytical systems to optimally monitor the transportation system performance.

*Milestone:* Complete design and integration of analytical system-August 2002.

### **Task 6: Partnership Building and Outreach**

This task will develop relationships with community partners and the necessary memorandums of understanding (MOU) among the various parties involved in the project and its implementation.

*Milestone:* Complete partnership agreements for Phases 2 and 3-July 2002; Assess community views on risks and benefits-September 2002.

**Hydrogen from Biomass for use in Urban Transportation  
Clark Atlanta University**

Task Designation/Milestone	FY2002					2003
	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4	Qtr 1
<b>Task 1: Feed Supply, Process Economics and Development</b>						
Development of models and solutions				◆		
Solubility and physical property estimations					◆	
Process design and economics of process flow sheets						◆
<b>Task 2: Reactor Modifications and shakedown</b>						
Design and construction of pilot scale pyrolyzer			★			
Shipping and integration/interfacing of fluidized-bed reformer at Scientific Carbons				★		
Shakedown of the integrated system					★	
<b>Task 3: Long-Duration Testing at Scientific Carbons</b>						
Complete 100-200 hours of integrated operation					★	
<b>Task 4: Preparation</b>						
Complete design of storage and utilization system					◆	
<b>Task 5: Environmental and Technical Evaluation</b>						
Complete design and integration of analytical system					◆	
<b>Task 6: Partnership Building and Outreach</b>						
Complete partnership agreements for Phases 2 and 3					◆	
Assess community views on risks and benefits					◆	

FY2002 Begins October 1, 2001

★ = Critical Milestone

◆ = Milestone

## **Hydrogen Production Through Electolysis – PROTON Energy Systems**

In PROTON Energy Systems' original proposal, work in Phase II was to focus on demonstrating PROTON's UNIGEN<sup>®</sup> regenerative fuel cell technology. This technology, once matured, will enable PROTON<sup>®</sup> electrolyzer hardware to work in both directions—as both an electrolyzer making hydrogen and as a fuel cell converting that hydrogen back into electricity. There are many advantages of an integrated unit that makes hydrogen, stores it at pressure and then reverses the flow to make power as needed.

As PROTON Energy Systems looks at what was learned during the Phase I activity and how to proceed to the Phase II it is clear to us that the electrolyzer is the key to a successful deployment. As the future unfolds, regardless of which renewable technology provides the electricity to make the hydrogen or which technology converts the hydrogen back into electricity, all require that the electrolyzer be reliable and inexpensive. Numerous companies are currently at work on the various methods of renewable electricity (e.g. Dish/Stirling, PV, Wind) and energy conversion (e.g. fuel cells, engines), but few companies are working on the most difficult and most critical link to a fully integrated renewable system, the electrolysis system.

PROTON's main objective for FY2002 will be to take what was learned on the HOGEN<sup>®</sup> 40 electrolyzer cost reductions and apply them to the HOGEN<sup>®</sup> 380 electrolyzer. In addition, PROTON Energy Systems will continue to advance work on the HOGEN<sup>®</sup> 40 cell stack as well as some additional studies on other HOGEN<sup>®</sup> 40 cost reduction opportunities. They will do this by focusing cost reduction efforts on some key elements of the HOGEN<sup>®</sup> 380 electrolyzer, the power electronics, the electrical controls and software, and the drying of the hydrogen gas. Most cost reductions realized on the HOGEN<sup>®</sup> 40 electrolyzer have yielded results that can be seamlessly implemented on the HOGEN<sup>®</sup> 380; others will only be realized through higher volume production. Those areas of cost reduction that are affected by production volume will be clearly identified and understood as part of the 2002 effort. PROTON Energy Systems will utilize in-house test systems to verify any new hardware or software developed for the HOGEN<sup>®</sup> 380.

### **Task 2.0: Cell Stack Cost Reduction**

#### **Task 2.1: Support Components**

The electrolysis cell stack has traditionally used machined endplates and a spring washer configuration on tie rods to maintain proper mechanical compression on the individual cell components. Work was done to compare machined metal endplates to endplates produced through a casting process in 2001. The effort in 2002 will focus on the cost reduction of the mechanical compression mechanism for the cell stack.

#### **Task 2.2: Process Improvements/Standardization**

Many of the processes used in manufacturing the cell stack components have involved highly skilled laboratory technicians operating in tightly controlled environments. In order to effectively and efficiently increase the volume production capability in the cell manufacturing, a rigorous process standardization effort is required. This effort will utilize Design of Experiments and Statistical Process Control techniques to identify process variation and develop techniques for process scale-up. These efforts will be used in developing machinery and equipment for high volume cell manufacture as production volumes increase.



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**Task 3.0: Power Conditioning and Renewables Interface****Task 3.1: Power Electronics**

The goal of this task is to look for innovative ways to reduce the cost of the cell stack power supply and associated electronics as well as improving its efficiency. Overall system efficiencies such as number of cells vs. current will be investigated in order to determine the optimum cost per kW PROTON Energy Systems can provide. Design work will look to integrate many of the parts of the current power electronics design into the two systems to eliminate redundant framework and components. In an effort to improve efficiency multiple designs will be investigated to ensure that the selected power supply is taking full advantage of the numerous technical advances in the power electronic field. Work on the HOGEN<sup>®</sup> 40 system power electronics was completed in FY2001. The effort for FY2002 will focus on the HOGEN<sup>®</sup> 380 power electronics section and take advantage of the cost reduction areas realized on the HOGEN<sup>®</sup> 40.

**Task 3.2: Alternate Energy Inputs**

The effort on the renewables interface in FY2002 will focus on gathering data from Illinois Institute of Technology on the HOGEN<sup>®</sup> 40/PV integration project which will utilize a renewable interface module developed in FY2001.

**Task 4.0: System Cost Reductions****Task 4.1: Circuit Board**

The goal of this task is to evolve the control board that was developed in FY2001 for use on the HOGEN<sup>®</sup> 40 and further develop it for use on the HOGEN<sup>®</sup> 380 electrolyzer. The control board will be used as the primary process controller and will be also utilized to provide remote connectivity and diagnostics capability.

**Task 4.2: Component Cost Reductions**

The main focus of this task for the HOGEN 380 is to evolve the gas dryer and dryer manifold concept developed for the HOGEN 40 into the larger scale HOGEN 380. The task is complicated by the fact that the HOGEN 380 is designed for outdoor use and thus a much greater temperature and humidity band to design within.

**Task 5.0: Manufacture Cost Reduced Design****Task 5.1: Test Items on HOGEN<sup>a</sup> 380**

This program does not have a task to build a brand new HOGEN 380 unit, nor is that prudent given the state of these cost reduction tasks. Proton has several test stands and early demonstration systems to test hardware and software advances and verify functionality and integrity.

**Hydrogen Production Through Electrolysis  
Proton Energy Systems, Inc.**

Task Designation/Milestone	FY2002					2003
	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4	Qtr 1
<b>Cell Stack Components</b>						
Complete Compression hardware Evaluation			◆			
Complete Chemical Process Standardization				◆		
<b>Power Electronics</b>						
Investigate Power Supply Options for HOGEN 380		◆				
Complete Cost Trade and Preliminary Design			★			
<b>Power Conditioning and Renewables</b>						
Collect Data on Alternative Input Integration From the HOGEN 40				◆		
<b>Circuit Board</b>						
Preliminary Design and Verification of HOGEN 380 Control Board			★			
Complete Validation of HOGEN 380 Control Board					◆	
<b>System Cost Reductions</b>						
Complete Full Validation of FY2001 Cost Reductions for System		★				
Complete Cast Component Cost Evaluation on HOGEN 40			◆			
Advance HOGEN 40 Gas Dryer into HOGEN 380 Design				★		

FY2002 Begins October 1, 2001

★ = Critical Milestone

◆ = Milestone

## **Renewable Hydrogen System Integration and Performance Modeling – Desert Research Institute**

This project has developed and tested a renewable energy fuel cell (REF) system for off-grid power applications. The system is composed of solar panels (2 kW), wind turbines (3 kW), inverter (4 kW), electrolyzer (5 kW), batteries, hydrogen storage tank, fuel cell (2 kW), programmable load bank (5 kW), computer system for data acquisition and component control, and electronic components (Snyder, 2000). The operation of the REF system is controlled by the computer and is designed to provide the power required by the load bank utilizing power from the solar panels, wind turbines and/or the fuel cell. A major emphasis of this project was to develop a computer system to evaluate inputs from approximately twenty-five sensors and utilize this information to control the entire system, including the fuel cell. The basic logic is that the electrolyzer generates hydrogen during times when excess solar and wind energy is available and then the fuel cell utilizes this hydrogen to produce electricity when there is insufficient solar and wind energy. The REF system functions very well in the Reno, Nevada, environment, which has a good balance of solar and wind energy throughout the year.

Four major market conditions must be resolved before systems such as the REF system can be commercially viable, viz., safe, reliable, ease of use and competitive energy costs. The major focus of this project was minimizing the users interface with the system and developing control for safe reliable system operation, because without a system that was self-managed and controlled, most users would avoid its use because of the complexity and time required to operate it. The system needs to appear seamless to the user so that the exact source of energy at any particular time is not known and no system adjustments are required if power consumption increases or decreases. Inappropriate owner intervention can also resulting unintended damage to expensive components, therefore a system that functions with minimal user input is desired.

The technical feasibility of the present control system was demonstrated successfully during this past fiscal year in a controlled operating environment. The next step is to prove safe, reliable, and user-friendly operation under “real world” operating conditions. This is the proposed objective for the next fiscal year.

### **FY 2002 Tasks**

#### **Task 1: Specify, purchase or lease and integrate new fuel cell system**

The fuel cell purchased by DRI for use in the integrated fuel cell system did not prove to be reliable for this application. The project was completed using a fuel cell borrowed from LANL. This borrowed fuel cell will need to be replaced and returned to LANL. A new fuel cell will allow the program to demonstrate the performance of newer designs and materials.

##### **Task 1a: Specify and purchase or lease a fuel cell**

It is anticipated that a robust fuel cell will be required for the project and therefore a new fuel cell that can be integrated into the system needs to be specified and purchased or leased.

##### **Task 1b: Integrate the new fuel cell into the existing system**

To integrate a new fuel cell into the existing structure, the compatibility of the electrical system as well as the cooling system and hydrogen and air input systems must be evaluated and made to work with the new stack.

**Task 2: Refine existing software**

The existing software performed in an exemplary manner, but still has some limitations before it can be applied in a completely stand-alone mode.

**Task 2a: Self-diagnosis and self-performance tuning**

A system that can provide self-diagnosis of problems or pending problems is extremely valuable in a complex, multi-component system. This is a relatively straight-forward operation because all pertinent parameters are captured with the current system, and software needs to be developed to flag individual or groups of parameters that go outside of expected values. For example, if the data acquisition system (DAS) senses an individual cell voltage below a set value, a purge sequence would be initiated to correct the low cell voltage. Self-tuning of the fuel cell to obtain optimal performance under a prescribed load is important to obtain the most electricity per unit volume of hydrogen.

**Task 2b: Develop and test software to handle unique conditions and use weather forecast data to condition system operation**

It is important to test the total system performance under rather extreme conditions of rapidly changing power consumption or production. The current system is able to handle rather large fluctuations, but extreme changes are what generally cause a system to fail, and it is important to determine what conditions the system is not able to handle and redesign the software to accommodate these conditions.

**Task 3: Collect performance data under different load application**

The current system was tested under a standard summer and winter residential load. There are other off-grid applications that could be anticipated such as farm/ ranch or business applications that need to be evaluated.

**Task 4: Explore how to reconfigure the system to increase efficiency and cost-effectiveness**

The current system components were purchased and installed based on availability and general capability, and not because they could produce optimal performance or cost-effective power.

**Task 4a: Use simulation model to reconfigure the system components to optimize system efficiency**

A TRNSYS computer model will be developed for the purpose of evaluating component and system reconfiguration to optimize system efficiency in terms of watts per dollar. Experience gained this past year has shown that the electrolyzer is oversized and the hydrogen storage tank is undersized. For example, further study is required to fully understand the contribution of the batteries to system control and reliable operation. An evaluation of various options will be modeled using TRNSYS yielding a proposed optimal configuration recommendation for various extreme climatic conditions.

**Task 4b: Explore ways to reduce parasitic losses and other inefficiencies**

During FY2001 major steps were taken to reduce parasitic losses by replacing the old blower system with a new, higher efficiency unit and other similar changes. There are other improvements that can be implemented to increase overall system efficiency and use the maximum amount of solar and wind energy produced. For example, there is no current limiting capability for the electrolyzer. Controlling the current to the electrolyzer will allow its operation with excess power generated from the wind and PV.

**Task 5: Hazard Assessment**

During the project an approved laboratory specific safety plan that meets all OSHA standards was prepared for operating the system in the Energy Lab. However, planning and installation of such a system at a residence or business requires a completely new review of all hazards and how they could be mitigated in such an installation. This hazard assessment will be undertaken during this fiscal year.

**Renewable Hydrogen System Integration and Performance Modeling  
Desert Research Institute**

Task Designation/Milestone	FY2002					2003
	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4	Qtr 1
<b>Task 1: Specify, purchase or lease and integrate new fuel cell system</b>						
1a: Specify and purchase/lease new fuel cell						
1b: Integrate new fuel cell into existing system			★			
<b>Task 2: Refine existing software</b>						
2a: Self-diagnosis and self-performance tuning						
2b: Develop and test software for unique conditions and use weather forecasts						
<b>Task 3: Collect performance data under different load applications</b>						
<b>Task 4: Explore how to reconfigure the system to increase efficiency and cost-effectiveness</b>						
4a: Evaluate how system components could be reconfigured or resized to improve performance						
4b: Reduce parasitic losses and inefficiencies						
<b>Task 5: Hazard Assessment</b>						

FY2002 Begins October 1, 2001

★ = Critical Milestone

◆ = Milestone

## **Hydrogen-Based Utility Energy Storage System – SRT Group, Inc.**

SRT Group, Inc. (SRT) has assembled a dedicated team to propose the demonstration and subsequent commercialization of a novel means for storing energy from electricity that is supplied from renewable resources. This approach is also applicable to electrical energy storage needs in other scenarios, such as distributed power, and cost effective load management without needing standby or peak generation facilities. Furthermore, the technology can be used for producing by-product hydrogen.

The system is based on using electricity generated during periods of low demand to electrolyze hydrobromic acid (HBr) into hydrogen (H<sub>2</sub>) and bromine (Br<sub>2</sub>). During high demand periods the hydrogen and bromine are recombined in the same unit, acting as a fuel cell, to regenerate the electricity. By careful scheduling of charging and discharging phases, energy storage by the system can obviate the need for expensive peaking generation units. As the system does not emit any waste products such as CO<sub>2</sub>, wastewater, or solid waste, permitting issues are eased, and the system can be situated near the load, saving the need to expand generating, transmission, and switching capacity solely to meet peak generating requirements.

Team member National Power PLC is currently working on a regenerative HBr/H<sub>2</sub>Br<sub>2</sub> fuel cell that has been designed for high volume, low cost manufacturability. This cell is expected to cost \$350 per kilowatt in production quantities.

The SRT system is also capable of being integrated with patented SRT hydrogen production system, which will allow simultaneous energy storage and hydrogen production for merchant and captive hydrogen markets and for producing clean-burning hydrogen fuel when hydrogen fueled vehicles become available. Thus, the SRT technology will link the emerging deregulated electrical industry and hydrogen vehicle fuel into a synergistic energy market.

Phase I work will include overall system design. In Phase I a 50 kW non-regenerative electrolyzer will be placed into the system to allow for testing as the regenerative cell is brought to completion using the data evolved. Subsystem testing and minor development of the bromine tank, control system and ancillary systems are included. System and operating safety parameters will be developed and applied throughout Phases I and II: from inception of system design to final construction and operation. In Phase II the non-regenerative electrolyzer will be replaced with a 100 kW regenerative cell and the system will be tested further. From the test data, a preliminary economic analysis will be preformed. In Phase III the size of the regenerative cell will be upgraded to 350kW with a production ready unit, which will be tested for long duration for commercial applications. The program will emphasize intrinsic safety, simplicity, redundancy, reliability, as well as suitably low cost.

Along with safety, cost and performance, a market analysis will be an essential component in assuring the commercial acceptance and success of the SRT system. The success of this technology will be sensitive to emerging and changing markets. This will be especially the case in the anticipated future of deregulated electrical utilities and clean-fuel vehicles. SRT's business plan will incorporate the latest market trends, projections and analysis using advanced computer software.

SRT has assembled a strong team of industry partners committed to developing this technology in the near to mid term. The team includes SRT Group Inc.; National Power, PLC, (NP) a worldwide Independent Power Producer based in the United Kingdom and the developer of bromine-based regenerative fuel cell; Electrosynthesis Company Inc., (ESC) producers of systems using electrolyzers and fuel cells, as well as engineering services; and Performance Solutions Group, Inc. (PSG) a business consulting organization. With such strong industrial financial backing and expertise, the SRT Team is well positioned to take advantage of future demand for both clean electricity and clean fuels.

**FY 2002 Tasks:****Task 3.0: 50 kw electrolysis system**

The 50 kw electrolysis system built in FY 2001 will be inspected and maintained while awaiting installation in the test stand

**Task 4.0: Build Test stand, Install and Checkout**

The 50 kW test stand will be constructed and the 50 kW electrolyzer will be placed into service and tested. Testing will involve determination of projected electrode lifetimes, achievable current density and optimum operating parameters.

**Task 5.0: Safety Analysis**

A safety analysis including a risk assessment for the testing will be performed.

**Task 6.0: Facility Preparation**

The ESC facility will be prepared to accept the test skid and perform the testing. Modifications include addition of high power electrical infrastructure, and explosion proof electrical wiring in preparation for hydrogen generation.

Hydrogen Based Utility Energy Storage System SRT Group, Inc.						
Task Designation/Milestone		FY2002				2003
	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4	Qtr 1
<b>Task 3.0: 50 kW Prototype Electrolysis System (ship unit)</b>					★	
<b>Task 4.0: Test Stand (T/S), Unit, Install, &amp; Checkout</b>					◆	
Task 4.5: T/S Fabrication					◆	
<b>Task 5.0: Safety Analysis</b>				◆		
Task 5.2: Evaluate fabrication of test stand installation				◆		
<b>Task 6.0: Facility Preparation</b>		◆				
Task 6.1: Insure all safety mech in place		◆				

FY2002 Begins October 1, 2001      ★ = Critical Milestone      ◆ = Milestone

## **HYDROGEN INFRASTRUCTURE**

### **Filling Up With Hydrogen 2000 – Stuart Energy Systems**

Under the program “Filling Up With Hydrogen 2000” hydrogen vehicle re-fueling systems, called fuel appliances will be developed in a prototype development program, which builds on Stuart’s new CST electrolysis technology. The fuel appliance combines the components needed to convert water and electricity to high-pressure hydrogen gas. The system consists of an electrolyser, compressor and refueling dispenser packaged in one or more easy-to-deploy units. The fuel appliance systems can be built to suit a wide range of hydrogen supply capacities, from the size needed to fuel a single vehicle over night, a unit Stuart calls a Personal Fuel Appliance (PFA) to larger service stations, named Packaged Hydrogen Supply Appliances, which can support many vehicles, including large fleets of buses.

#### **Task 1: Personal Fuel Appliance (PFA)**

The second working model, P1 Model 25, producing up to 50 SCFH at 3600 psig, was built and successfully tested. The unit was delivered to Ford Motor Company in FY Q2 2001 as part of a joint evaluation program to run the next 24 months. Beyond the joint project with Ford, a number of other units based on the P1 Model 25 will be built and will be supplied to other auto industry partners. The exchange of technical information on performance of these prototypes will complete this task.

#### **Task 2: Packaged Hydrogen Supply Systems**

Testing of the P3-1A fuel appliance prototype has been underway since FY Q3 2000 at SunLine Transit at their bus garage in 1000 Palms CA. P3-1A produces 1500 SCFH at 4000 psig and is based on Stuart’s multi-stack CST electrolyser technology. Operating responsibility for the unit will be handed over to SunLine’s Operations group at the beginning of FY Q1 2002. Field-testing of the unit will continue until the end of FY Q2 2003.

The two P3-1B prototypes are complete and under test. Both prototypes feature Stuart’s single stack CST electrolyser technology, producing up to 400 SCFH. P3-1B LP, which ran for 2700 hours at Stuart’s test facility, was dismantled, the condition of the stacks evaluated. To remedy low current efficiency the stack was redesigned. The unit will be rebuilt with the new stack design, and the compressors will be upgraded to 600-psig maximum pressure. It is expected that the unit will be ready for field-testing at the end of FY Q1 2002. The proposed field application is fueling metal hydride storage tanks aboard underground mining vehicles.

The second prototype, P3-1B HP which produces gas at up to 5,000 psig, has been under field test at Powertech Laboratories, Surrey B.C. since FY Q2 2001 and has accumulated over 1000 hours running time. The unit will continue to test at this location until the end of FY Q2 2003. A second P3-1B HP unit will be built in FY Q4 2001 and delivered to the California Fuel Cell Partnership to be a satellite filling station located at AC Transit, Richmond CA.

The P3-5 prototype 5-bus fueller was taken to the design stage, and a prototype cell assembly was built. Construction of the P3-5 fueller was abandoned because of a lack of a suitable field test site.

Construction of the P4-1A, a 400 SCFH fueller demonstrating Stuart’s P4 process, is well underway. The unit is expected to be complete and under factory test by the end of FY Q1 2002. P4-1 B, a more refined version of this prototype, is expected by the end of FY Q2 2002. At the same time construction of P4-10, a 10-bus fueller, will begin in FY Q2 2002, with the design and construction of the cell stack expected by the end of FY Q3 2002.



**Filling up with Hydrogen 2000**  
**Stuart Energy Systems**

Task Designation/Milestone	FY2002					2003
	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4	Qtr 1
<b>Task 1. Personal Fuel Appliance</b>						
Annual Report PFA Evaluation				◆		
<b>Task 2. Packaged Hydrogen Supply Appliance</b>						
Hand over P3-1A to SunLine Operations		◆				
Complete Rebuild of P3-1B LP			◆			
Annual Report P3-1B HP at Powertech				◆		
Deliver second P3-1B HP unit to AC Transit			★			
Start testing of P4-1A		★				
Complete Design/Build a cell stack for P4-10				◆		
Complete Design/Build of P4-10 Appliance						★

FY2002 Begins October 1, 2001

★ = Critical Milestone

◆ = Milestone

### **Light, Medium Duty Fleet – NRG Technologies**

NRG Technologies will bring clean, high-performance light to medium-duty vehicles using hydrogen fuels to market by achieving the following objectives:

- Develop a cost-effective, low-emissions retrofit package for light to medium-duty vehicles that seamlessly converts existing natural gas and/or gasoline engines to hydrogen-enriched fuels.
- Exceed CARB SULEV standards for 2003 using the Supplemental Federal Test Procedure (SFTP). Previous work by NRG Technologies has shown the following emissions levels. Carbon monoxide (CO) emissions will be undetectable (<1ppm); non-methane hydrocarbon (NMHC) emissions will be <0.05 g/hp-hr; and oxides of nitrogen (NO<sub>x</sub>) will be <0.15 g/hp-hr. Depending upon the driving cycle, these values represent an 85% reduction in NO<sub>x</sub> emissions alone when compared to the standard.
- Maintain or enhance current vehicle drivability, durability and operating range by effective selection, matching, and configuring of off-the-shelf components.
- Prove and enhance the retrofit package design through in-service testing.
- Develop a public/private partnership to implement a commercialization plan that will bring new business and economic opportunities to Nevada.

#### **Task 10: In Service Testing**

Implementing the test plan developed in Task 4, NRG will manage the collection of data, both objective and subjective, for the operation of the two retrofitted vehicles.

#### **Task 11: Final Vehicle Emissions Testing**

Following in service testing of each retrofit package, the two vehicles will be returned to CAVTC. Here the driving tests will be repeated to determine the reliability of the emissions control technology.

<b>Light, Medium Duty Fleet NRG Technologies</b>						
<b>Task Designation/Milestone</b>		<b>FY2002</b>				<b>2003</b>
	<b>Qtr 4</b>	<b>Qtr 1</b>	<b>Qtr 2</b>	<b>Qtr 3</b>	<b>Qtr4</b>	<b>Qtr 1</b>
Task 7: Finalize Retrofit Package Design	◆					
Task 8: Installation and Emissions Verification of Retrofit Packages		◆				
Task 9: Federal, State and Local Approvals		◆				
Task 10: In Service Testing				◆		
Task 11: Vehicle emissions Testing				◆		
Critical Milestone: Verification of Vehicle Performance		★				

FY2002 Begins October 1, 2001      ★ = Critical Milestone      ◆ = Milestone

## **Hydrogen Commercialization for the 21<sup>st</sup> Century – SunLine Services Group**

This project is designed to transpose Department of Energy funded research and development (alpha site) technology in the area of hydrogen fuel development to the next level in the process of full commercialization (beta site) infrastructure development. The project aims to generate hydrogen, from the renewable resources of solar and wind energy, to fuel a growing cluster of vehicles in the Coachella Valley Clean Cities Region.

During FY 2000/2001, SunLine Services Group (SSG) completed (1) integrating the Hydrogen Burner Technology Natural Gas Reformer into the current system for producing hydrogen from natural gas; and (2) construction of the base supports and superstructure for the photovoltaic tracking arrays from EcoEnergies. SSG continued for the second year operation and maintenance a fleet of hydrogen powered vehicles – three fuel cell golf carts, one Neighbor Electric Vehicle, and one hydrogen ICE. (The hydrogen ICE was leased to Startech Environmental for one year of testing.) Hydrogen vehicles added to the fleet were the XCELLSiS PEM Fuel Cell ZEBus and two ICE Hythane® Buses. SSG continued to operate and maintain two differing types of electrolyzers: (1) a Stuart Energy Systems electrolyzer that produces 1400 standard cubic feet (scf) of hydrogen per hour and (2) a Teledyne Brown electrolyzer that produces 40 scf of hydrogen per hour. During this reporting period, SunLine has given tours to over 5,000 visitors from countries around the world of its hydrogen generation, compression, storage and dispensing facilities in a "customer friendly atmosphere." Documentation and reporting of hydrogen production and usage is continuing. All SunLine personnel have been trained in hydrogen and SSG personnel have been trained in operation and maintenance of hydrogen equipment. Development of a training curriculum to support the equipment and vehicles, as well as the various power train configurations, is in process.

### **FY2002 Tasks:**

**Task 1:** Maintenance and operation of the Teledyne Brown electrolyzer, Stuart Energy's P3 electrolyzer, compressors, solar flat plat arrays, solar tracking panels and the electrical equipment required to operate the hydrogen production and fueling facility at SunLine shall continue in year 3 of this project.

**Task 2:** SunLine shall continue to maintain and operate the hydrogen storage and dispensing systems contained in this project.

**Task 3:** Maintenance and operation of the hydrogen-fueled vehicles is an on-going activity at SunLine.

**Task 4:** Data collection, documentation and analysis of every aspect of the production, compression, storage and dispensing of hydrogen shall continue at SunLine.

**Task 5:** The support services for this project include delivery of hydrogen fuel to the City of Palm Desert, education with public tours and presentations, and follow-on training in the operation, maintenance and repair of all of the hydrogen related equipment.

Future work includes the completion of a safety assessment of the hydrogen complex and implementation of a hydrogen-from-wind project. Three wind turbines at Wintec wind farm will operate a Stuart Energy electrolyzer; hydrogen will be transported to SunLine for use in vehicles and a stationary fuel cell.

**Hydrogen Commercialization for the 21<sup>st</sup> Century  
SunLine Services Group**

Task Designation/Milestone	FY2002					2003
	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr4	Qtr 1
Maintenance and Operations				◆		
Data Collection and Analysis				◆		
Support Services				◆		
Documentation and Reporting	◆				★	
Safety Assessment		★				
Wind Energy		◆			◆	

FY2002 Begins October 1, 2001

★ = Critical Milestone

◆ = Milestone

## **Hydrogen and Fuel Cell Vehicle Evaluation – National Renewable Energy Laboratory**

The primary goal of this Hydrogen project is to gather performance information on hydrogen fuel cell vehicles (including light, medium, and heavy-duty vehicles) to establish their operating characteristics and applicability to fleet service and the general transportation marketplace. Additionally, this project will gather and evaluate information on establishing a hydrogen fueling and vehicle maintenance infrastructure.

A secondary goal of the project will be to evaluate the comparable performance and operation of transit buses using Hythane (20% hydrogen & 80% natural gas) versus natural gas as a fuel.

The project objectives for FY2002 are:

- NREL will continue the relationship with SunLine Transit Agency and AC Transit to define the hydrogen fuel cell bus evaluation process and required fueling infrastructure at the AC Transit site.
- NREL will evaluate the performance and operational characteristics of a hydrogen fuel cell bus in revenue service at SunLine Transit Agency.
- NREL will establish an effective relationship with the California Fuel Cell Partnership (CaFCP) and define the added value tasks we can provide to their fuel cell vehicle testing and evaluation program.

Government and industry-sponsored research on using hydrogen as a transportation fuel, particularly in mobile fuel cells is growing rapidly. One of the first applications for fuel cells in the transportation arena will be in powering transit buses, due to their capacity for handling the extra volume currently required for the fuel cell and the associated hydrogen fuel-storage tanks. Preliminary studies of fuel cell buses have been carried out at Georgetown University and by the Chicago Transit Authority and have appeared to be positive; however, additional testing and evaluation will be necessary before the buses will be widely accepted by the transit industry.

The CaFCP is a focal point for fuel cell development and demonstration activity. One of the tasks of the Partnership will be to evaluate fuel cells used in transit bus applications. SunLine Transit Agency and AC Transit Agency, both located in California and associate members of the Partnership, will each be acquiring fuel cell buses for evaluation in normal operation. However, the buses will not be delivered until 2003. In the interim, a prototype XCELLSiS fuel cell bus has been operated by the manufacturer at SunLine Transit Agency for a period of time to gain experience and knowledge of fuel cell performance and operation characteristics. Unfortunately, the XCELLSiS bus is scheduled to leave SunLine in September 2001, before allowing NREL the opportunity to characterize its performance.

A new prototype fuel cell bus from ISE Research is scheduled to be at SunLine for approximately 6 months beginning in late CY2001. During that period, NREL will assist SunLine in acquiring data to evaluate the bus performance to prepare the agency for eventual delivery of their fully commercial fuel cell buses.

The California Fuel Cell Partnership (CaFCP) is also evaluating fuel cells in light-duty vehicles, looking at a variety of feedstock fuels for the hydrogen normally required for the fuel cells. Individual automobile manufacturers, who are members of the partnership, are accomplishing preliminary testing of their vehicles in the Sacramento, California area, preparing them for eventual release to the consumer market. Acceptance of these vehicles into the market will be affected by the perceived added value and viability of the technology. Third-party evaluation of the vehicles will be necessary to establish the credibility of manufacturers' claims.

**Task 1: Process Definition**

Coordinate with SunLine and AC Transit to further define and document the process for collecting and evaluating performance and operational data on the fuel cell buses, which will be initiated upon the delivery of the buses from the manufacturer. In addition, NREL will characterize the infrastructure modifications that are required to fuel and maintain the vehicles at each site.

**Task 2: Performance Characterization**

Characterize the performance and operation of the ISE Research fuel cell bus to be tested at SunLine starting in late 2001/early 2002.

**Task 3: Role Definition**

Define the role that NREL can play in the evaluation of light and medium-duty fuel cell vehicles associated with the CaFCP.

Hydrogen and Fuel Cell Vehicle Evaluation NREL						
Task Designation/Milestone		FY2002				2003
	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4	Qtr 1
<b>Task 1: Process Definition</b>						
Define AC Transit Hydrogen Bus Infrastructure					★	
<b>Task 2: Performance Characterization</b>						
Preliminary evaluation results					◆	
<b>Task 3: Role Definition</b>						
Complete meetings with individual CaFCP members and document results in a memo to the NREL Hydrogen Program Manager				◆		

FY2002 Begins October 1, 2001      ★ = Critical Milestone      ◆ = Milestone

## **Hydrogen Reformer, Fuel Cell Power Plant and Vehicle Refueling System – Air Products and Chemicals, Inc.**

Air Products and Chemicals, Inc., in partnership with Plug Power Inc. and the City of Las Vegas (CLV), Nevada, will develop a facility to serve as a commercial demonstration of hydrogen as a safe and clean energy alternative for stationary power production and vehicle refueling. The project objectives are:

- 1) The development and demonstration of small-scale, on-site hydrogen production technology;
- 2) The design and installation of a hydrogen and hydrogen/compressed natural gas (CNG) blend refueling facility in Las Vegas, Nevada;
- 3) The development and installation of a stationary, hydrogen-fueled, 50-kW PEM fuel cell system (FCS) at the CLV to be performed by Plug Power Inc.

The project consists of the following technical tasks:

### **Task 1: Design and Development**

An existing hydrogen generator prototype will be tested to ensure its design, operation and system capabilities for integration with the FCS and the fuel station at the CLV site. A scaled-up hydrogen generator of sufficient capacity to meet the future demands at the CLV site will be designed based on the test results of the prototype. This generator will be sufficient to meet the hydrogen demand of the planned heavy-duty and light-duty hydrogen and hydrogen-enriched natural gas fleet vehicles, the 50 kW fuel cell system, and a potential 100 kW blended hydrogen/natural gas stationary engine/generator.

A 50 kW PEM FCS will be designed and developed. All aspects of integration of the FCS with the hydrogen production and compression system, and the integration of the FCS with site grid power will be worked out to arrive at a suitable FCS design.

A hydrogen and hydrogen/natural gas blend-fuel station will be designed to closely resemble the state-of-the-art in CNG fueling. The hydrogen generator(s) and 50 kW PEM FCS will be incorporated into this refueling station. A detailed design for the integration of the various subsystems will be completed to ensure that the components function smoothly as a total system.

### **Task 2: Construction and Installation**

Initially (Phase 1), Air Products and CLV will install a fueling system to provide sufficient hydrogen to enable operation of three light-duty vehicles and the DOE H<sub>2</sub> hybrid electric bus. This system will consist of a merchant (liquid) hydrogen supply system, and the compression, blending, and fuel transfer equipment. In Phases 2 and 3, this fuel station will be integrated with the prototype, and subsequently the scaled-up hydrogen generators.

The prototype hydrogen generator will be moved from Allentown, Pa., reinstalled, and tied in to the 50 kW FCS, and fuel station at the CLV site. As the demand for hydrogen is anticipated to grow, a scaled-up hydrogen generator will be assembled, installed, and integrated with the fuel station and the other loads at the site.

The 50 kW FCS will be assembled and tested at the Plug Power facility in Latham, N.Y., installed at the CLV site, and connected with the hydrogen generator and fuel station subsystems.

### **Task 3: Systems/Station Integration**

Permitting and safety review activities will be performed to install and operate the system at the site.

Start-up and testing of the subcomponents to ensure proper operation will be completed. CLV, with assistance from Air Products and Plug Power, will operate and maintain the facility, ensuring that all subcomponents operate together as a whole and that the system has the highest level of availability and reliability.

**Plans for FY 2002**

The initial fueling system will be installed and on-stream (29 Oct 2001). This system comprises a merchant liquid hydrogen supply system, and the compression, blending, and fuel transfer equipment.

The fully tested prototype hydrogen generator will be moved from Allentown, Pa. to Las Vegas and installed with the fuel station (29 Oct 2001). This unit will then be integrated with the fuel station and brought onstream (30 Nov 2001). This activity is the critical milestone in the schedule.

The fully assembled and tested 50 kW fuel cell system will be shipped to Las Vegas to be connected with the hydrogen generator and fuel station (29 Oct 2001). This unit will then be integrated with the fuel station and brought onstream (30 Nov 2001).

The scaled-up hydrogen generator assembly will be completed (29 Oct 2001) to begin a planned testing program in the vendor's shop. Testing will be completed (31 Dec 2001), and the unit will be moved to Las Vegas, installed, integrated with the fuel station and brought onstream (28 Feb 2002).

Air Products, CLV, and Plug Power will conduct the start-up testing of the various subcomponents after installation at the site. They will ensure that all subcomponents operate together as a whole and that the system has the highest level of availability and reliability. Reliability data from the various subcomponents will be gathered, and the need for any corrective actions will be determined. Valuable experience will be gained on the usage patterns of the fuel station, and on the ease of use of the fuel-dispensing systems, which will indicate if any modifications need to be made in the later phases of operation.



Hydrogen Reformer, Fuel Cell Generator, and Vehicle Refueling System Air Products and Chemicals						
Task Designation/Milestone		FY2002				2003
		Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4
<b>Task 1: Design and Development</b>						
<b>Reformer Design Development</b>						
Complete Prototype Generator Testing		◆				
Complete Design of scaled-up commercial hydrogen generator			◆			
<b>50 kW PEM Fuel Cell</b>						
Complete Design of 50 kW PERM Fuel Cell system		◆				
Assembly complete			◆			
Performance Test complete at Plug Power				◆		
<b>CLV Vehicle Refueling Station</b>						
Design of Vehicle Refueling Station completed		◆				
Deliver equipment to site		◆				
<b>Task 2: Construction and Installation</b>						
Commission Refueling Station in Las Vegas (based on liquid hydrogen supply source)		◆				
Commission Hydrogen Generator at CLV Refueling Station		★				
Commission 50kW PEM Fuel Cell at CLV Refueling Station		★				
<b>Task 3: Systems, Station Integration/Operation</b>						
Demonstrate integrated operation of the Refueling Station						

FY2002 Begins October 1, 2001      ★ = Critical Milestone      ◆ = Milestone

## **Hydrogen Composite Tank Program – Quantum Technologies, Inc.**

In fiscal year 2001, the Department of Energy contracted with Quantum Technologies to develop advanced ultra-lightweight, all-composite storage tank technology for on-board motor fuel storage of hydrogen. This tank technology was based on QUANTUM's TriShield all-composite storage tank technology, which incorporates a thermoplastic liner that acts as a permeation barrier for the hydrogen. The tank technology also incorporates a composite overwrap which acts as a structural shell that provides the cylinder with its strength. The third layer is an impact-resistant outer shell, which protects the tank in accident and crash situations.

DOE's stated target of 8.5% minimum hydrogen by weight (34.5 MPa, 300K) was technically challenging, especially for a smaller diameter (11 inch) pressure vessel. QUANTUM utilized in-house expertise and resources to perform all required design, development, fabrication and validation testing of composite pressure vessels. Additional materials expertise was obtained from Toray Carbon and Thiokol Propulsion, our strategic partners.

Other technologies for hydrogen storage, such as room temperature metal hydrides are limited to just over 1% hydrogen by weight. Direct high pressure storage offers the advantages of simplicity, efficiency and cost-effectiveness.

QUANTUM's current designs have been successfully tested in severe crash tests (direct impacts on dome, straight cylindrical section and ends, while cylinder is at low pressure: 300 psi) and long term durability tests imposed by major automotive OEMs.

In order to achieve the 70% improvement in storage efficiency required in the present solicitation, without sacrificing (a) damage tolerance and durability required in automotive applications and (b) hydrogen permeation barrier properties, three-pronged approach was utilized:

- Optimize metallic hardware for weight efficiency;
- Optimize liner material and process to improve weight and volume efficiencies; and
- Optimize composite shell (design and process) to improve weight and volume efficiencies.

The challenge in optimizing metallic hardware was the limitations imposed in material selection due to hydrogen embrittlement. QUANTUM relied heavily on finite element analysis (ANSYS) and wealth of experience within QUANTUM and Thiokol Propulsion (manufacturer of NASA Space Shuttle Solid Rocket Boosters). Thiokol provided QUANTUM access to over 800 engineers, decades of hydrogen fuel management experience to optimize weight of metallic hardware.

The challenges in optimizing the thermoplastic liner were the limitations imposed in material selection and design due to high and low temperature performance requirements, permeation resistance and processability. QUANTUM utilized the in-house capabilities to mold plastic liners using various material options based on considerable experience in various thermoplastic material options including metalized thin liners. QUANTUM also utilized in-house facilities to perform high and low temperature evaluations and permeation assessment.

In order to improve the composite shell efficiency, QUANTUM adapted: (1) higher strength reinforcing fiber (2) an improved resin impregnation system that maximizes the translation efficiency of the fiber (3) toughened epoxy system that will help maintain the damage tolerance of the composite shell in spite of the reduction in wall thickness.

QUANTUM worked very closely with Toray Carbon--the world's largest carbon fiber supplier and has access to their research facility in Ehime, Japan, and discussions are underway to supply a higher strength

fiber for application in hydrogen storage tanks. QUANTUM has in house capability to design, fabricate and test composite pressure vessels efficiently and quickly. QUANTUM is experienced in certifying pressure vessels to US ANSI/AGA NGV2 regulatory requirements.

QUANTUM has worked closely with General Motors and Exponent Failure Analysis Associates since 1994 to develop validation requirements for CNG cylinders. Failure Modes and Effects Analysis (FMEA) results from this program and QUANTUM's extensive experience in gaseous fuel management provide important inputs for the proposed hydrogen storage program.

QUANTUM also has developed a partnership agreement with Thiokol Propulsion for access to their considerable technical resources in materials, process, testing and hydrogen gas management.

### **Proposed Project Review (FY 02):**

Again for this coming year, QUANTUM proposes to work on projects related to the DOE objective to demonstrate high performance pressure vessels to be used with hydrogen in OEM mobile applications such as cars or buses. The tanks and integrated supports have to meet rigorous industry standards and specifications while maintaining price competitiveness.

While developing new tank sizes for a service pressure of 5,000 psi, QUANTUM is highly interested to design, develop and validate 10,000 psi vessels. A number of major OEMs are now very interested in direct pressurized hydrogen storage rather than on-board reformation because of cost reduction, durability, technology and emissions reasons. QUANTUM has had numerous requests by world's major OEM's for 10,000 psi technology. The technologies developed with the collaboration of DOE are extremely critical enablers for the FC vehicle marketplace, since vehicle range and safety are critical components to widespread commercialization of hydrogen internal combustion engine and hydrogen fuel cell vehicles. 10,000 psi technology must be developed, demonstrated and evaluated to determine the potential prospects for widespread commercialization. QUANTUM will be undertaking these projects in close association with Thiokol, as a strategic partner and major subcontractor.

### **Phase II Continuation: Design, Development, Validation and Delivery of Future Truck 5,000 psi tanks**

QUANTUM is planning to design & develop a new tank size for the Future Truck competition 02. The design & development will be based on an existing 18"x28" tank. A high strength, high efficiency composite shell, filament wound using advanced reinforcing materials, will be developed to provide maximum strength at the lowest possible weight. The tank will have a new in-tank regulator developed by QUANTUM.

### **Phase TBD: Design, Validation and Delivery of Future Truck 5,000 psi Integrated supports.**

QUANTUM plans to design, validate and deliver integrated supports for the Future Truck 5,000 psi tanks. The Fuel Storage system including the tank with in-tank regulator and integrated supports will be designed for installation on a current OEM vehicle. The integrated supports will be evaluated based on the vehicle OEM design specifications.

This phase is dependant upon the completion of Phases 1 and 2.

### **Phase VI & VII: Design, Development and Validation 10,000 psi tank.**

QUANTUM Technologies is planning the extension and optimization of the 5,000 psi H<sub>2</sub> (dimension TBD) tank to achieve a 10,000 psi H<sub>2</sub> storage pressure. Design and development would include:

Selection and screening of new, advanced materials for liner fabrication to withstand 10,000 psi operating pressure without creep, permeability and compression set.

Advanced stress analysis and optimization scheme to maximize load carrying capability of structural fibers.

### Phase TBD: Fuel Cell Bus Fuel Storage Integration

QUANTUM is proposing to apply our considerable expertise in gaseous fuel storage and fuel handling to develop a safe and reliable integrated fuel storage module for the DOE Nevada Fuel Cell bus.

<b>Hydrogen Composite Tank Program</b> <b>Quantum Technologies, Inc.</b>						
Task Designation/Milestone		FY2002				2003
	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4	Qtr 1
<b>Design, Development, Validation and Delivery of Future Truck 5,000</b>						
Size TED 5,000 psi tank development			★			
Size TED 5,000 psi tank Validation			◆			
<b>Design, Validation and Delivery of Future Truck 5,000 psi Integrated Supports</b>						
Integrated Supports Validation			◆			
<b>Design, Development and Validation 10,000 psi tank</b>						
Tank Development			★			
Tank Validation				◆		
<b>Fuel Cell Bus Fuel Storage Integration</b>						
Subsystem Design			◆			
Subsystem Installation					◆	

FY2002 Begins October 1, 2001      ★ = Critical Milestone      ◆ = Milestone

## **Insulated Pressure Vessels for Vehicular Hydrogen Storage – Lawrence Livermore National Laboratory**

The purpose of this project is to design, analyze, construct and test low-temperature, high-pressure gaseous hydrogen storage vessels. These vessels should be capable of handling temperatures as low as 20 K and pressures as high as 34.4 MPa (5000 psi). These vessels have packaging characteristics similar to those of conventional, low-pressure liquid hydrogen tanks, with much reduced venting losses. Compared with liquid hydrogen, cryogenic high-pressure hydrogen gas gives increased flexibility to the fueling infrastructure, since the vehicle can be fueled with liquid hydrogen, with high-pressure hydrogen cooled with liquid nitrogen, or with ambient-temperature hydrogen. Other forms of hydrogen storage exist, but they have their limitations. Hydride storage is heavy, and compressed hydrogen requires a very large volume.

This project aims to develop and demonstrate a near-term storage technology that can satisfy light duty vehicle storage needs in a cost effective way. The insulated pressure vessel can be used in light duty vehicles, storing 5 kg of hydrogen and resulting in a long range (640 km), low weight (30 kg), and low external volume (140 liters), and no hydrogen losses due to venting under all but the most extreme conditions.

Other advantages of insulated pressure vessels are:

1. They can reduce the total requirement for liquid hydrogen, because they have the potential to use ambient-temperature-compressed hydrogen under most conditions. Liquid hydrogen may only be used when a long range is required.
2. Insulation requirements are significantly reduced from those of a liquid hydrogen tank. This reduces the cost and the thickness of the insulation. As a result, the external volume of a cryogenic pressure vessel is likely to be lower than the external volume of a conventional liquid hydrogen tank.

**Task 1:** LLNL will build 6 full-size (130 liter internal volume) insulated pressure vessels according to LLNL's current design.

**Task 2:** LLNL will test LLNL's vessels according to the remaining DOT standards. These include the drop and bonfire tests.

**Task 3:** LLNL will do 100 cryogenic cycles on the pressure vessels for determining safety at low temperature.

**Task 4:** LLNL will subject the pressure vessels to cryogenic tests according to the SAE Standards. The cryogenic tests are the drop test and the bonfire test.

**Task 5:** LLNL will work on installing two of the full-size pressure vessels on demonstration vehicles to be operated at SunLine transit, with cooperation and participation from Structural Composites Industries (SCI). Completion of this task requires that LLNL obtain timely complementary funding from the South Coast Air Quality Management District.

**Task 6:** LLNL will study the procedure and the requirements for achieving DOT or SAE certification for cryogenic-compatible pressure vessels and generate a draft document proposing a set of rules for certification. Completion of this task requires that LLNL obtain timely complementary funding from the South Coast Air Quality Management District.

**Insulated Pressure Vessels for Vehicular Hydrogen Storage  
Lawrence Livermore National Laboratory**

Task Designation/Milestone	FY2002					2003
	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4	Qtr 1
Build 6 pressure vessels according to our current design	◆					
Test our vessels according to the remaining DOT standards. These include the drop and bonfire tests.		◆				
<b>Key Milestone:</b> Do 100 cryogenic cycles on the pressure vessels for determining safety at low temperature.				★		
Subject the pressure vessels to cryogenic tests according to the SAE Standards. The cryogenic tests are the drop test and the bonfire test.					◆	
Install two of the full-size pressure vessels on demonstration vehicles to be operated at SunLine transit, with cooperation and participation from Structural Composites Industries (SCI).						◆
Study the procedure and the requirements for achieving DOT or SEA certification for cryogenic-compatible pressure vessels and generate a draft document proposing a set of rules for certification.						◆

FY2002 Begins October 1, 2001

★ = Critical Milestone

◆ = Milestone

## **Mine Locomotive and Loader Projects – Sandia National Laboratories**

These projects have the following broad goals:

- (1) Demonstrate the feasibility of using hydrogen fuel cells for tractive power in underground applications.
- (2) Demonstrate enhanced performance of fuel cell power plants over other available technologies for underground use (batteries, tethered, diesel).
- (3) Demonstrate a potential intermediate niche market for fuel cells (1000 - 2000 per year).

These broad goals are to be accomplished with partners in the mining industry, mine vehicle manufacturers and mine safety regulatory agencies in the U.S. and Canada.

There are two immediate objectives to meet in order to achieve these broad goals. The first is the development and evaluation of a fuel cell-powered mining vehicle, specifically, a 4-5 ton electric drive locomotive designed for use in mines and tunneling operations. The project is a joint venture between U.S.D.O.E., CANMET (Canada) and private industry in Canada and the U.S. This unit is the first fuel cell powered locomotive and the first fuel cell powered vehicle developed for heavy duty underground applications. Sandia's role is the development and fabrication of a fuel cell-hydride power plant for the vehicle.

The second objective is the development of a fuel cell powered loader. This project is a significant step up in level of difficulty because it will require a power plant with energy storage and power requirements approaching an order of magnitude larger than the locomotive. The project is expected to take three years for completion.

The two tasks are described below:

### **Task 1: Mine Locomotive**

As reported in the program review, Sandia's engineering effort was increased significantly beyond the original project description because of a number of factors – (a) unavailability of the SRL hydride beds from the hydrogen bus, (b) delivery by Nuvera of fuel cell stacks without the balance-of-plant equipment required for their operation, (c) changes in the power plant configuration requested by the partners, (d) necessity to perform the integration of the power plant with the locomotive and, (e) new requirements dictated by MSHA (Mine Safety and Health Administration) and the Canadian MOL (Ministry of Labor) for underground operation. These factors have necessitated a much larger effort than anticipated and has resulted in a late delivery schedule for the equipment.

In spite of these issues, the power plant was completed and integrated with the locomotive in FY01. Furthermore, initial tests have been performed on the locomotive system to verify operation and these have provided considerable data on the power plant performance under load from the locomotive motor and control system. However, no test track was available and these tests were performed with the locomotive wheels raised off the short track section supplied by the manufacturer. There are two tasks, which must be completed before the final phase of the locomotive project (underground performance evaluation) can be completed. These are (1) making the required changes to the assembly dictated by the safety regulators (MSHA) to allow its use underground and, (2) perform on-track performance tests. An additional task to be completed involves the development of a refueling method and system. However, this work will be performed by other project participants under the loader project, using the locomotive as a prototype for the larger vehicle. The two subtasks are as follows:

A: Mine hardening of power plant and locomotive assembly

As mentioned above, some modifications will be required in order for the vehicle to be allowed to operate underground. These required changes are currently being defined by MSHA in collaboration with Sandia and the Canadian MOL.

B: Surface testing of locomotive

Surface testing and evaluation of the locomotive will be performed in Reno, Nevada at an ore site facility. Following shipment of the locomotive to the test site, Sandia's role will be to (a) supply training and consultation on the power plant/locomotive operation, (b) perform modifications or repairs as needed during the tests, (c) establish a refueling manifold and provide training in its use and, (d) provide consultation on the tests and a comparison with existing data taken at Sandia.

**Task 2: Loader Project**

The primary objective of this task in FY02 will be to perform an engineering analysis and write a specifications document for the loader power plant. This phase 1 work will lay the foundation for developing a power plant, which will meet the requirements of the DOE and the industry partners. Final design and fabrication is expected to begin in FY03. The work will consist of the following subtasks:

A: Define power plant requirements

Work with the loader supplier (Caterpillar) to compile power plant requirements, including space constraints, power requirements, duty cycle, safety requirements, ergonomics, shock vibration, temperature, humidity, service intervals, and operations schedules.

B: Determine fuel cell stack requirements

Evaluate fuel cell stack performance through bench testing and define requirements for the fuel cell balance of plant.

C: Hybrid modeling

Perform modeling and analysis tradeoffs for hybrid power supply and motor options in collaboration with Southwest Research Institute and Caterpillar.

D: Develop conceptual layout for loader power plantE: Identify interface requirements

Identify interface requirements to hydride bed, couplings, coolant loop, hydrogen sensors and motor controller.

F: Write specifications document for power plant, including:

- space constraints for each of the following subsystems: fuel cells, balance of plant, hydrogen supply, additional batteries, controls system, coolant loops and sensors
- environments for each of the subsystems
- performance specification
- control systems
- power specifications
- motor controls
- duty cycle

G: Write project plan for power plant fabrication and testing for FY03



**Mine Locomotive and Loader Projects  
Sandia National Laboratories**

Task Designation/Milestone		FY2002					2003
		Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4	Qtr 1
<b>Mine Locomotive</b>							
Complete mine hardening			◆				
Ship locomotive to Nevada			★				
<b>Loader Project</b>							
Complete stack measurements				◆			
Complete conceptual layout					◆		
Complete project plan							★

FY2002 Begins October 1, 2001

★ = Critical Milestone

◆ = Milestone

## REMOTE POWER

### Power Parks System Simulation Project – Sandia National Laboratories

Sandia National Laboratories is developing a system model to simulate distributed power generation in power parks, where power generation is co-located with a business or an industrial energy consumer. Due to deregulation, aging infrastructure, and local power shortages (as experienced recently in California), distributed power generation is gaining interest nationwide. Power parks can be sited as a node on the electric grid in areas where local energy use or geographical factors make an alternative energy source practical. Proposed power parks might use combinations of technologies, such as photovoltaic (PV) collectors, wind turbines, gas micro-turbines, and fuel cells fed by hydrogen generated by electrolysis or hydrocarbon-fueled reformers. Power parks provide an excellent opportunity for hydrogen technologies to contribute to generation of energy from renewable resources.

The deliverable of the project will be a tool for simulation of the local power generation system, constructed in the language of the Simulink software. Sandia National Laboratory will develop a library of individual components for hydrogen production, storage, and utilization to generate electricity, along with components representing internal loads and electric distribution to the grid. These modules can then be extracted from the library to construct a system model for a specific power park. The Simulink software allows the components to be coupled in block diagram format, convenient for varying the configuration of the park. Dynamic simulations will predict the performance of the power park subject to variations in system parameters. Variations in the system design can be evaluated to optimize the power production and minimize energy consumption. Previous work at Sandia performed simulations for remote-area power systems consisting of a fuel-reformer, a fuel cell, and a hydrogen storage system to meet a load cycle.

The final stage of the work will implement a control strategy to direct the power within the park to balance meeting internal load with external power supply. Previous experience with energy analysis of residential systems (S. R. Vosen, J. O. Keller, *Int. J. Hydrogen Energy*, 1999; 24: 1139-1156) showed that the control strategy affects the optimal design of the components, especially those related to energy storage; intelligent control allowed division of energy between storage options that yielded a system with lower-cost and higher efficiency.

**Task 1:** Develop a library of Simulink modules for the various components being proposed for power parks. Expected components include a PV array, a micro-turbine, a fuel cell stack, hydrogen generators (electrolyzer and hydrocarbon reformer), hydrogen storage, and an internal load.

**Task 2:** Assemble the components into a sample power park. The sample park will be based on existing or proposed parks, but not dedicated to a specific facility. The energy use within the park will be based on a sample industrial process with sufficient generality in the definition of a load function that the results and experience gained will be useful for understanding other cases.

**Task 3:** Evaluate performance of the power park. Run dynamic system simulations over a variety of conditions to analyze the energy efficiency and ability of the park to meet internal load.

**Task 4:** Implement a control system to direct the power to internal loads, storage components, or the external grid for optimum performance.

**Power Parks System Simulation Project  
Sandia National Laboratories**

Task Designation/Milestone		FY2002					2003
		Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4	Qtr 1
Task 1. Develop library of Simulink modules for power park components				◆			
Task 2. Assemble the component modules for a sample power park				★			
Task 3. Evaluate system performance of the power park						◆	
Task 4. Implement a control algorithm to optimize power park							◆

FY2002 Begins October 1, 2001

★ = Critical Milestone

◆ = Milestone

### 3.3 Analysis and Technology Transfer

This element includes projects in the areas of analysis (process, systems, and integration) and in the transfer of technology both domestically and internationally. Projects are being undertaken at universities, national laboratories, and in industry.

The analysis area is made up of projects involving analysis of technology development and validation processes, analysis of integrated systems, and integrated analysis of major components of the overall program. The systems analysis area consist of environmental, economic, and market analyses of potential hydrogen energy systems, their subcomponents, and the supporting infrastructure, as shown in Table 3.6. The products of these analytical studies will be used by the DOE Program Manager to establish program priorities for R&D as well as for near-, mid-, and long-term component, subsystem, and system validations.

Table 3.6 Analysis Projects		
<b>Goals:</b>		
<ul style="list-style-type: none"> <li>• <b>Ensure that Federal R&amp;D investments in hydrogen production, storage, distribution, and end-use technologies will provide the maximum value added to national strategic goals including global greenhouse emission mitigation;</b></li> <li>• <b>Identify and evaluate key market segments and market entry conditions for hydrogen utilization in transportation and in electricity generation at distributed and remote locations; and</b></li> <li>• <b>Develop and apply metrics to measure the Program's contribution to attaining national strategic energy goals and market share in key market segments.</b></li> </ul>		
Category	Project	Researchers
<i>Analysis Activities</i>	Process Analysis of Hydrogen Research Activities	National Renewable Energy Laboratory
	Distributed Hydrogen Fueling Systems Analysis	Directed Technologies, Inc.
	Hydrogen Technical Analysis	Arthur D. Little Inc.
	Inventory and Gap Analysis of Federally Funded R&D	National Renewable Energy Laboratory
	Big Sky Fuel Cell Program Commercial applications for Stationary Fuel Cells	CTA Energy Solutions
	Hydrogen Infrastructure Coordination	National Renewable Energy Laboratory

## ANALYSIS ACTIVITIES

### **Process Analysis of Hydrogen Research Activities – National Renewable Energy Laboratory**

The goal of this effort is to provide direction, focus, and support to the development and introduction of hydrogen through evaluation of the technical, economic, and environmental aspects of hydrogen production technologies. Broadly speaking, two analysis methods are used to affect this work. First, technoeconomic analyses (TEA) are performed to determine the potential economic viability of a research process. Second, life cycle assessment (LCA) is used to evaluate the environmental benefits and drawbacks of the process. TEA allows us to determine the likelihood that a process now at the research level will be economically competitive with conventional systems. Most importantly, however, this tool is used to identify research areas that could result in cost reductions. Using LCA, the environmental benefits of hydrogen technologies can be quantified and integrated with the economics of the process.

This year, analyses will focus on improving the understanding of the technical issues involved with integration of hydrogen research technologies into a large-scale hydrogen transportation market. The degree of benefits and opportunities for processes that produce hydrogen from sunlight, wind, and biomass will be studied. Additionally, efforts will be started to improve the predictive capabilities of a model that determines the cost of hydrogen storage and transportation.

#### **Task 1: Assessment of Natural Gas Splitting with a Concentrated Solar Reactor**

Review economic analysis performed on this project in FY01, and conduct a life cycle assessment on the process, to determine the net greenhouse gas benefits over steam methane reforming.

#### **Task 2: Assessment of the market potential of coproducts from biomass pyrolysis oil**

Review the possible coproducts from the reforming of biomass pyrolysis oil. Determine the market size and geographic distribution, as well as historic value.

#### **Task 3: Evaluation of water requirements for large-scale hydrogen use**

Determine the amount of water that would be required to produce enough hydrogen for various levels of transportation market sector penetration. Assume both conventional and renewable technologies for hydrogen production. Compare results to water requirements for other operations and markets (e.g., pulp and paper mills, recreation, municipal supply).

#### **Task 4: Monte Carlo analysis of storage and transportation costs**

Using the model developed by W. Amos in 1998, perform a Monte Carlo analysis on hydrogen storage and transportation costs. Using a standard deviation from the assumptions used in the model, determine the parameters that most highly affect cost results.

**Process Analysis of Hydrogen Research Activities  
National Renewable Energy Laboratory**

Task Designation/Milestone		FY2002					2003
		Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4	Qtr 1
<b>Task 1: Assessment of Natural Gas Splitting with a Concentrated Solar Reactor</b>							
Report				★			
<b>Task 2: Assessment of the market potential of coproducts from biomass pyrolysis oil</b>							
Report			◆				
<b>Task 3: Evaluation of water requirements for large-scale hydrogen use</b>							
Report					◆		
<b>Task 4: Monte Carlo analysis of storage and transportation costs</b>							
Report						◆	

FY2002 Begins October 1, 2001

★ = Critical Milestone

◆ = Milestone

## **Distributed Hydrogen Fueling Systems Analysis – Directed Technologies, Inc.**

During FY 2001 DTI completed the second year of a three-year contract to evaluate additional details regarding the major fuel options for fuel cell vehicles: hydrogen, gasoline and methanol. The specific tasks for FY 2001 included a comparison of steam methane reforming with partial oxidation/autothermal reforming of natural gas at stationary fueling sites, and a comparison of various gas cleanup options for those same stationary fueling systems. The tasks for FY 2002 have been altered from our original proposal based on new developments. In the original plan we projected working on a laboratory demonstration of small-scale steam methane reformers in addition to analyzing renewable hydrogen options. However, in the intervening years, DTI has independently funded the development of the small scale reformers, which led to the formation of a new company specifically to develop, manufacture and sell low-cost hydrogen fueling appliances. Since DTI has already built operational 1/3 scale reformers based on our proprietary technology, they have recommended to the Program Manager that the last year of the three-year grant be shifted exclusively to evaluating renewable hydrogen options.

Assuming that funding is received, DTI plans on completing these tasks during FY 2002:

### **Task 1. Evaluate the cost of producing hydrogen from biomass in the Midwest**

- Estimate the cost of hydrogen produced by gasifying switchgrass in the Midwest farming states.
- Compare the economics of utilizing that hydrogen for on-farm vehicles and appliances via fuel cells, vs. the economics of converting the hydrogen to electricity via fuel cells or via gas turbines and exporting the resulting electricity.

### **Task 2. Evaluate the cost of producing hydrogen from wind energy in the Midwest**

- Analyze hydrogen costs produced by electrolyzing water in farm areas of the Midwest utilizing wind energy, taking into account the peak-shaving and storage attributes of hydrogen.

### **Task 3. Compare the cost of transmitting energy from the Midwest to urban areas by electricity with the costs by shipping hydrogen in pipelines**

- Compare the costs of transmitting wind energy as electricity vs. the cost of converting wind energy to hydrogen and transmitting and distributing that hydrogen by pipeline, including the costs of local hydrogen distribution.
- Compare the costs of transmitting hydrogen produced by gasifying switchgrass via pipeline with the costs of converting the hydrogen to electricity and transmitting the electricity by the electrical grid.

**Distributed Hydrogen Fueling Systems Analysis  
Directed Technologies, Inc.**

Task Designation/Milestone	FY2002					2003
	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4	Qtr 1
<b>Task 1: Cost of Producing Hydrogen from Biomass</b>						
Literature Review			◆			
Biomass Hydrogen Cost Summary Report				◆		
<b>Task 2: Cost of Producing Hydrogen from Wind</b>						
Literature Review				◆		
Wind Hydrogen Cost Summary Report					◆	
<b>Task 3: Comparative Energy Transmittal Costs</b>						
Literature Review					◆	
Energy Transmittal Summary Report						◆
Final Report						★

FY2002 Begins October 1, 2001



= Critical Milestone



= Milestone



## **Hydrogen Technical Analysis – Arthur D. Little, Inc.**

The Department of Energy has been working in a variety of areas associated with most of the hydrogen supply chain – production, storage, and utilization. However, one area that consistently receives only moderate attention throughout the hydrogen community is the purification of the hydrogen produced. While some efforts are being expended on absorption systems and certain membrane systems at the fundamental level, very little attention has been paid to the requirements for integration into small-scale hydrogen production systems and the effect they have on overall system efficiency, complexity, and cost. This is of concern as many of the projected uses of this hydrogen (e.g. fuel cells) have rather stringent requirements for hydrogen purity. Nevertheless, no hydrogen infrastructure can be built without the technology.

Given the importance of hydrogen purification technologies, and in the interest of ensuring a balanced approach promoting the development of technologies and policies that encourage the widespread use of hydrogen, we have focused the effort in this study on reviewing hydrogen purification technologies not currently funded by DOE. Specifically, we have investigated what hydrogen purification technologies are being developed (or should be developed) and how they fit with the existing and emerging production technologies on one hand and with existing and emerging storage and end-use technologies on the other.

Under last year's funding, Arthur D. Little (ADL) reviewed hydrogen purification technologies and assess them in the context of different raw hydrogen production technologies (small-scale SMR and ATR), storage technologies (pressurized tanks and physical media), and utilization technologies (hydrogen ICE vehicles and fuel cell vehicles). The three most promising non-DOE funded purification technologies were selected for detailed analysis based on their potential for overall system improvements in hydrogen selling price and/or primary energy use efficiency. The three most promising purification technologies selected were non-palladium metal membranes, fluorinated metal hydrides (dry), and fluorinated metal hydride slurries. ADL determined that small-scale PSAs were an appropriate baseline for comparison purposes. A detailed analysis, requiring the development of an overall system cost/performance model, was performed on each purification technology with the various fueling station options. The model includes a description of the production, storage/transportation, and utilization modules based on in-house information, and developer and DOE input as appropriate. Based on the results of the model analysis and discussions with purification technology developers, ADL will prepare a final report summarizing our results in FY2002.

### **Task 5: Preparation of final reports**

In this task we will summarize the results from each technology analysis in a presentation-style summary report. The analysis results will include a characterization of the technology (performance, maturity, risks, cost), comparison to conventional methods, potential niche markets/applications, and recommendations for future development. The submittal of this draft documents will be the critical milestone in our schedule. Finally, we will submit a final report summarizing our results to DOE.

**Hydrogen Technical Analysis  
Arthur D. Little Inc.**

Task Designation/Milestone		FY2002					2003
		Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4	Qtr 1
<b>Task 5. Preparation of Final Report</b>							
Draft report to DOE		★					
Final report to DOE		◆					

FY2002 Begins October 1, 2001

★ = Critical Milestone

◆ = Milestone

## **Inventory and Gap Analysis of Federally Funded R&D – National Renewable Energy Laboratory**

The objective of this project is to develop a comprehensive inventory of federally funded hydrogen energy research, development and demonstration projects. Searches of available databases will be conducted and will be used to develop a single database of hydrogen energy projects. Careful review of this database and grouping of projects based on research focus will provide a comprehensive inventory of hydrogen activities. This inventory will then be used to identify duplication of effort and gaps in the federal hydrogen portfolio.

Inventory of all federally funded hydrogen research and development is essential for minimizing duplication of effort and identifying research gaps. The Rand Corporation has developed (for the Office of Science and Technology Policy) a comprehensive annual database of ongoing research and development sponsored by the 24 federal agencies. Using the Research And Development In the United States (RADIUS) database, which compiles the submissions of all federal agencies work (down to the task level), NREL has completed a search of the activities related to hydrogen energy RD&D for FY1999 and compiled these into a single database. This inventory will be used as a baseline for tracking funding trends and identifying gaps in the federal R&D portfolio.

The five-tiered boxology that was developed last year will be refined, as appropriate, to reflect emerging technology developments. Searches of available databases, including RaDiUS and USDA Current Research Information System (CRIS), will be performed to obtain FY2000 funding information. Efforts will also begin on capturing data for FY2001. All records will be incorporated into the Access database and categorized based on the boxology. A comparison to the FY1999 portfolio will be made. Gaps and duplication of effort will again be identified. A skills assessment will be performed to identify national expertise in the technical areas where gaps in the hydrogen R&D portfolio are identified. Finally, efforts will be made to tabulate the state and local hydrogen energy activities for FY1999-2001.

Inventory and Gap Analysis of Federally Funded Hydrogen R&D NREL						
Task Designation/Milestone	FY2002					2003
	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4	Qtr 1
Complete FY2000 Searches			◆			
Report for DOE Review					★	

FY2002 Begins October 1, 2001      ★ = Critical Milestone      ◆ = Milestone

**Big Sky Fuel Cell Program Commercial Applications for Stationary Fuel Cells – CTA  
Energy Solutions**

*Information not available at the time of printing.*

## **Hydrogen Infrastructure Coordination– National Renewable Energy Laboratory**

The goals of this project are to coordinate all infrastructure development activities for the DOE Hydrogen Program, including activities of other DOE programs, other federal agencies, state and local governments, industry, and public interests groups, and to create a central focus, information source, and coordinating function for hydrogen infrastructure development and deployment in the U.S. and in other key countries.

The project objective for FY02 is to prepare and distribute a draft National Hydrogen Infrastructure Development Plan based on the Blueprint for Hydrogen Fuel Infrastructure Development to help guide DOE Hydrogen Program activities in infrastructure development.

Interest and investments in hydrogen energy technologies have increased noticeably over the past year. The DOE Hydrogen Program needs a mechanism to track and coordinate a number of activities involving the development and deployment of hydrogen infrastructure.

### **Task 1: Codes and Standards**

Coordinate hydrogen codes and standards activities in the U.S. for the DOE Hydrogen Program. Key activities include:

- serving as a technical advisor to the International Code Council's Hydrogen Ad Hoc Committee
- working with the National Hydrogen Association on both domestic and international codes and standards development, including the activities of the proposed Joint Working Group
- providing technical support to the Safety Committee of the DOE Hydrogen Technical Advisory Panel
- performing other work as necessary to ensure effective and timely development and promulgation of hydrogen codes and standards.

### **Task 2: Infrastructure**

Coordinate hydrogen infrastructure development activities for the DOE Hydrogen Program. Key activities include:

- creating a national information clearinghouse for hydrogen infrastructure development using NREL's extensive contacts with key stakeholders such as energy companies (fuels and electricity), industry associations, automotive companies and suppliers, public interest groups, other DOE programs and federal agencies, and state and local governments
- providing technical support to the DOE Hydrogen Program by preparing solicitations for competitively awarded subcontracts, reviewing and monitoring subcontractor activities and reports, and assisting DOE in making strategic RD&D investments to facilitate and accelerate infrastructure development
- planning, coordinating, and managing preparation of a government-industry National Hydrogen Infrastructure Development Plan that incorporates a national transportation fuel strategy developed with DOE/OTT and the energy and auto industries.

**Hydrogen Infrastructure Coordination  
NREL**

Task Designation/Milestone		FY2002					2003
		Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4	Qtr 1
<b>Task 1: Codes and Standards</b>							
Assist HTAP conduct Hydrogen Safety Summit				◆			
<b>Task 2: Infrastructure</b>					★		
Draft National Hydrogen Infrastructure Development Plan							

FY2002 Begins October 1, 2001

★ = Critical Milestone

◆ = Milestone

Table 3.7 Technology Transfer Projects		
Goal: Develop informed constituencies in the industrial and public sectors as part of a strategy to accelerate the commercialization of renewable hydrogen technologies		
Category	Project	Research
<i>Technology Transfer Activities</i>	Hydrogen Technical Analysis on Matters Being Considered by the International Energy Agency	Longitude 122 West Inc.
	Technical Analysis of Currently Funded Projects	Energetics, Inc.
	Strategic Planning and Implementation	National Renewable Energy Laboratory
	Outreach Activities	Sentech, Incorporated
	Outreach – Hydrogen Film	Hydrogen 2000
	Hydrogen Codes and Standards Outreach	National Hydrogen Association

## TECHNOLOGY TRANSFER ACTIVITIES

### Hydrogen Technical Analysis on Matters Being Considered by the International Energy Agency – Longitude 122 West, Inc.

The U.S. Department of Energy participates in various activities of the International Energy Agency (IEA) through an Implementing Agreement and its Annexes. Hydrogen Agreement Annex 13, "Design and Optimization of Integrated Systems," calls for the U.S. to participate in three integrated system teams. The three teams and their projects are:

- Remote Power Systems
- Home/Residential Systems
- Transportation Applications.

#### **Task: Annex 13 Participation and Independent Analysis**

Longitude 122 West serves as U.S. Team leader for Annex 13 activities. The work involves coordinating with the three integrated system teams, participating in strategy development, and performing independent hydrogen system analysis. The goal of the analysis is to provide independent modeling and assessment, especially of capital and operating costs, for the integrated systems.

The current emphasis is on spreadsheet modeling, to make comparisons between system configurations and technologies easier. Other factors being considered are efficiency (fuel economy) and environmental impact. Current emphasis is on Infrastructure to support Transportation Applications. Various sensitivity studies to assumed costs and operating parameters are underway. A draft and final report will be prepared.

In addition, Longitude 122 West attends expert meetings and interacts with the IEA Operating Agent at NREL. In FY2002, a Task development workshop will be held in the early spring, possibly in Mexico to encourage South American participation. Presentation of final results at the World Hydrogen Energy Conference in Montreal is planned. This task ends at the end of June 2002.

<b>Hydrogen Technical Analysis on IEA Matters Longitude 122 West, Inc.</b>						
Task Designation/Milestone		FY2002				2003
	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4	Qtr 1
<b>Independent Analysis and Annex 13 Participation</b>						
Attend Fall Experts meeting (Oslo, Norway)	◆					
Attend Annex 13 Task Development Workshop			◆			
Technical Analysis and Cost Modeling			★			
Attend World Hydrogen Energy Conference				◆		
Draft and Final Report		◆		◆		

FY2002 Begins October 1, 2001      ★ = Critical Milestone      ◆ = Milestone



## **Technical Analysis of Currently Funded Projects – Energetics, Inc.**

Energetics, Incorporated is working on a task that involves conducting technical analyses or evaluations of projects that are currently funded by the U.S. Department of Energy's Hydrogen Program. The analyses, conducted for the benefit of hydrogen stakeholders, are centered on a site-visit to the location of each of the projects designated by the Golden Field Office. These analyses address the feasibility of the project and how it contributes to making hydrogen a leading energy carrier in the 21<sup>st</sup> century. Energetics also is augmenting this effort by providing the stakeholder with expanded information coming from follow-up detailed technical analyses on key issues stemming from the site-visit analyses, and with a compilation of all hydrogen project site visit/analyses that Energetics has performed over the past five years under various contracts.

In addition, Energetics is augmenting the storage and stakeholder databases that were constructed last year, is adding a publications database to the package. The databases will be on the Hydrogen Web Page.

Energetics, if funding permits, also plans to develop a booklet describing the hydrogen related efforts of U.S. industry-based hydrogen stakeholders.

### **Task 1: Outreach Activities**

#### **1a. Site Visit-Based Reports**

Energetics will perform in-depth technical analyses on key projects currently being funded by the DOE Hydrogen Program. Once a project is chosen for technical assessment, a literature review will be performed on the subject. This will include a review of the last two or three years of Annual Operating Plan submittals, monthly reports, the Annual Review paper, published reviewers' consensus comments from the past few years, publications in journals, and journal publications on the same or similar topics by other researchers. Following completion of the literature review, the Principal Investigator (PI) will then be contacted, and an on-site visit arranged. A set of topic questions or discussion points will then be drawn up based on the literature review, and sent to the PI one to two weeks prior to the visit. The site-visit itself will include a presentation by the PI (formal or informal) on the project and its current status, a tour of the laboratory in which the project is being conducted, preferably including a demonstration of the experimental process(es), and detailed discussions based on the topic questions and on any other items that may come out of the tour, demonstration, and presentation. Following the meeting, Energetics will write a comprehensive report that will discuss the project in detail.

Year Two of the current contract began in July 2001, and calls for 13 site-visit analyses. Two will be completed prior to the start of FY 2002. The remaining eleven will be performed during FY 2002, and will be completed by July 2002. It is anticipated that Year Three of the contract will commence in July 2002, and the first three site visits of that year will be performed during the last quarter of FY 2002.

#### **Task 1b: Compilation of Site Visit Analyses 1995-2001**

Energetics will produce a document that will contain the report on each site-visit performed, starting in 1995 through the end of Year One of the current project (July 2001). The earlier reports will be reformatted to put them into the more streamlined style that has been developed. An introductory section will be written that will provide the stakeholder/reader with an overview of the entire series of evaluations to date, and will include a "where are they now" section on several of the projects that were among the earlier ones evaluated.

#### **Task 1c: Databases**

Energetics will update the Stakeholder and Storage databases that were previously developed. The Storage Database will also be augmented by the addition of information on technical publications produced by these stakeholders.

If funding permits, a Utilization Database similar to the Storage database will also be developed.

#### Task 1d: Industry Booklet

If funding permits, Energetics will develop a booklet on the U.S. hydrogen industry. The booklet will be modeled after a similar booklet on the Canadian hydrogen industry published by Natural resources Canada.

### **Task 2: Analysis Activities**

#### Task 2a: In-Depth Analyses on Projects Previously Visited

Energetics will perform in-depth studies (techno-economic analyses, feasibility studies, benefits analyses, or mass/thermal balance-based engineering calculations) on three projects. These analyses will be based on and performed in expansion of the work on three previous site visits from Year One, Year Two, or even earlier. A separate report will be provided for each of the analyses.

#### Task 2b: Niche Market Analyses

Energetics will complete analyses of two potential niche markets for hydrogen-related products. The first involves niche market systems that could feed fuel cells from metal hydride/hydrolysis-based hydrogen storage systems. The assumption is that the byproduct hydroxide is not recycled (the high cost component of these type of storage systems), but can either be sold or safely discarded. Several metal hydrides (e.g., calcium, sodium, magnesium) in various niche market scenarios (e.g., power lawn mowers, electric wheelchairs, etc.) will be evaluated.

Second, Energetics will complete an assessment of high temperature solid oxide-based electrolysis technology to develop cost and performance estimates of these systems and will compare them to both conventional alkaline electrolysis and PEM-based electrolysis. This will also include an analysis of SOFC technology to develop cost and performance estimates of SOFC systems for use in distributed generation applications.

#### Task 2c: Economic Analysis of Hydrogen-Blended Fuels

Energetics will continue an economic analysis on the benefits of hydrogen-blended fuels in stationary gas turbines. This work is being performed under contract to Sandia National Laboratories, and the description is included in Sandia's write-up.

**Technical Analysis of Currently Funded Projects  
Energetics, Inc.**

Task Designation/Milestone	FY2002					2003
	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4	Qtr 1
<b>Task 1: Outreach Activities</b>						
1a. Site visit-based reports						
Complete first two site visits		◆				
Complete nine site visits by the annual review				◆		
Complete 13 Site visits; write year two report					★	
1b. Compilation of site visit analyses 1995-2001						
Complete compilation			◆			
1c. Databases						
Stakeholder, storage, and publications databases ready to be inserted or linked to Hydrogen Web Page		◆				
1d. Industry booklet						
First draft completed				◆		
<b>Task 2: Analysis Activities</b>						
2a. In-depth analyses on projects previously visited						
Completion of 1 <sup>st</sup> , 2 <sup>nd</sup> , 3 <sup>rd</sup> analysis		◆	◆	◆		
2b. Niche market analyses						
Completion of metal hydride analysis		◆				
Completion of solid oxide analysis			◆			

FY2002 Begins October 1, 2001

★ = Critical Milestone

◆ = Milestone

## **Strategic Planning and Implementation – National Renewable Energy Laboratory**

The goals of this project are to coordinate strategic planning activities for the DOE Hydrogen Program, including interaction with the Office of Power Technologies (OPT) hydrogen vision and roadmapping activity; create a central focus, information source, and coordinating function for strategic planning in the DOE Hydrogen Program; and provide technical and administrative support to the DOE Hydrogen Technical Advisory Panel (HTAP).

The project objective for FY02 is to work with the DOE Hydrogen Program, HTAP, and OPT management to develop a 5-year Hydrogen Program Plan.

### **Task 1: Strategic planning**

Consolidate strategic planning activities in progress and those planned by the OPT, HTAP, and other key organizations for the DOE Hydrogen Program.

### **Task 2: Technical and administrative support for the DOE's HTAP**

Continue to assist DOE and HTAP plan and conduct meetings and other activities needed to carry out HTAP's advisory duties.

Strategic Planning and Implementation NREL						
Task Designation/Milestone		FY2002				2003
	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4	Qtr 1
<b>Task 1: Strategic planning</b>						
Draft 5-year Hydrogen Program Plan (with a 20-year outlook)					★	
<b>Task 2: Technical and administrative support for the DOE's HTAP</b>						
Semi-annual meetings of the HTAP		◆		◆		

FY2002 Begins October 1, 2001      ★ = Critical Milestone      ◆ = Milestone

## **Outreach Activities – Sentech, Inc.**

SENTECH, Incorporated (SENTECH) is focused on conducting Outreach and Communication activities for the Hydrogen Program. This effort is part of a three-year cooperative agreement award with the Department of Energy (DOE), Golden Field Office for technical analysis, which is entering the second year. SENTECH activities, as guided by this agreement will help to develop the communication tools necessary to effectively convey to multiple audiences the merits of hydrogen energy systems, their challenges, and their place in a sustainable energy economy.

The activities being pursued by SENTECH will compliment the research and development work funded by the DOE by presenting the technical achievements and validations of hydrogen energy technologies to non-traditional audiences. They will also raise the visibility of DOE's Hydrogen Program within these new audiences. The ultimate benefit of these activities will be to break the perceptual barriers - that hydrogen is unsafe, uneconomic, and of little benefit - commonly held by the uninformed. Additionally, the educational forum will help further DOE's commitment to "helping educate our nation's next generation of scientists, engineers, technicians, and educators."

### **Task (Golden Field Office): Technical Analysis**

#### **Subtask 1: Information analysis for communication brochures**

SENTECH will produce and distribute two glossy brochures that target the specific markets for hydrogen energy technologies. These markets, which have not yet been identified, will represent areas where near-term applications for hydrogen are possible. These brochures will answer the questions of safety, economics, and benefits by presenting examples of successful applications of hydrogen. The brochures will be distributed at two relevant technical conferences and through traditional distribution channels.

#### **Subtask 2: Industry meeting, analysis, and assessment**

SENTECH will conduct face-to-face meetings with a number of companies from select industry sectors that have a stake in the development of hydrogen as an energy carrier. The exact number of companies has not yet been determined although it is expected that 6-10 meetings would be possible. Presentations made to these groups will be tailored to their specific industries. Feedback will be incorporated into individual trip reports, and submitted as a deliverable.

The focus of these has changed from those conducted in previous years in an effort to include more visits to industries that may not be aware of hydrogen energy, technologies, applications, and benefits.

SENTECH will also target companies perceived as "on-the-fence" when it comes to making corporate commitments to hydrogen energy, as well as related industries that may play an important role in the development of the hydrogen energy infrastructure. The ultimate purpose of the meetings will be to educate and initiate a continuing dialog in the effort to promote hydrogen energy and address perceptual barriers.

#### **Subtask 3: Educational forums and assessments**

SENTECH will work with NHA and others to conduct two educational forums during the contract period. Last year, SENTECH, Inc. initiated an overhaul of the educational forums in an effort to improve the presentation of information using advanced communications technologies to reach even more schools and students.

The SENTECH will work to identify and contact candidate middle schools in the Washington, DC area, present information on the forum, and down select candidate participants. It is anticipated that the education forums will include hands-on activities for the students, child-safe experiments, and various stations where they can learn about hydrogen and hydrogen technologies. Additionally, it is expected that other program deliverable products will be included, such as: excerpts from the *Renewable Power* and

*Hindenburg* videos, a hydrogen lecture by some program participants, and a panel of experts assembled for a question and answer period with the students. All teachers involved in the educational forums will be mailed materials packets including the *Mission H2* CD-ROM and accompanying *Teacher's Workbook* to allow for an introduction to hydrogen through preparatory course work.

Outreach Activities Sentech, Inc.						
Task Designation/Milestone		2002				2003
	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4	Qtr 1
Produce two communication brochures			◆		★	
Complete ten industry outreach meeting and analysis of results			◆			
Complete two education forums			◆		◆	
FY2002 Begins October 1, 2001      ★ = Critical Milestone      ◆ = Milestone						

## **Outreach: Hydrogen Film – Hydrogen 2000**

Global warming - or climate change - has become one of the most hotly debated and contentious environmental issues of our time. The subject is complex and the ramifications are potentially severe. Much of the debate concerns the impact of human activity, and in particular the release of carbon dioxide, CO<sub>2</sub>, into the atmosphere by burning fossil fuels, versus natural phenomena out of our control. Even skeptics agree that the earth's atmosphere is warming, though they say that without proof that CO<sub>2</sub> emissions are the cause, efforts to curb carbon output will do more economic harm than environmental good. The questions revolve around specific aspects of the problem within that general agreement. How much will the atmosphere warm up? What will happen? To what extent are humans responsible? And what can and should we do about it?

The contractor shall research and develop a script and other pre-production elements for a one-hour length Hydrogen Program Education Outreach Documentary, with the working title, *The Hydrogen Age*. The audience is expected to be educated with an interest in science and policy issues. The goal is to develop a script/documentary, which is suitable for presentation on the Discovery Channel or the Public Broadcasting Service (PBS).

The contractor shall develop a content outline for DOE approval. Content shall be objective, balanced, and fact-based, and shall not overstate the issues, problems or solutions. To ensure this, the contractor shall enlist the assistance of knowledgeable advisors and technical experts in the field, as well as key sponsors to review and comment on proposed content.

Upon approval, the contractor shall proceed with full development of the script and other pre-production elements. The script shall present the issues of global warming through a balanced discussion of environmental, economic, technical, and political drivers and how they will likely impact the next fifty years. The script shall also showcase promising new energy technologies and demonstrate how humanity can meet our energy needs while stimulating economic growth and mitigating air pollution and global climate change. The script shall show how a "hydrogen-based energy economy" and the widespread adoption of fuel cell technology - as well as other technologies for energy efficiency and conservation - can allow society to move toward a more sustainable, pollution-free energy future. The script shall provide the audience a look at established and emerging economies around the world. [For example, developing countries like China and India have rapidly increasing populations with a matching demand for energy. Industrial economies in North America, Europe, and Japan are investigating ways to keep up with increased demand for energy while reducing emissions and environmental impacts. Developed and developing countries alike have an interest in efficient clean technologies. Some, such as Japan and Iceland, are seriously considering converting to a hydrogen- based (electric) energy economy.]

Deliverables for Task 5 shall include a content outline and script, both in draft and final.

<b>Outreach: Hydrogen Film Hydrogen 2000</b>						
<b>Task Designation/Milestone</b>		<b>FY2002</b>				<b>2003</b>
	<b>Qtr 4</b>	<b>Qtr 1</b>	<b>Qtr 2</b>	<b>Qtr 3</b>	<b>Qtr 4</b>	<b>Qtr 1</b>
Produce working script				★		

FY2002 Begins October 1, 2001      ★ = Critical Milestone      ◆ = Milestone

## **Hydrogen Codes and Standards Outreach – National Hydrogen Association**

**Technical Conference Support:** The NHA will hold technical conferences with industry, academia, national laboratories, government laboratories, code officials and code organizations to bring experts together in a focused activity to develop and write new standards for hydrogen technologies. This includes such items as storage tanks, fueling nozzles, connectors, safety equipment, and other key components and integrated systems needed to move hydrogen into the energy sector. The NHA has members and staff who are active participants in the International Standards Organization and its Technical Committee 197 who is responsible for the presentation and approval of the developed standards.

**ICC Codes Support:** The NHA will support the International Code Council in their efforts to review, develop and promulgate new codes for the use of hydrogen. This includes providing experts, technical reports, data and other information needed by the Code Officials to complete the development of these new codes. The NHA will attend any scheduled meeting of the ICC Ad Hoc Hydrogen Committee, and review available materials during the duration of this contract.

### **Schedule:**

The following bullets describe the NHA's approximate schedule for the two tasks proposed. Annual reports covering work in the prior fiscal year will be prepared.

#### **4Q01: Technical Conference Support:**

**TC 1** - The NHA will participate in at least one safety code and standards meeting in Detroit, Michigan, sponsored by the Society for Automotive Engineers (SAE) Fuel Cell Standards Safety working group.

**TC 2** - The NHA will work with organizers of the World Hydrogen Energy Conference (WHEC) to begin planning a technical presentation on hydrogen safety for WHEC scheduled for June 2002.

**TC 3** - The NHA will also conduct a meeting of the U.S. TAG members of ISO TC 197 in preparation for the 2001 Plenary meeting in Paris, France. The NHA will attend the plenary and related working groups, and serve as Chairman of the U.S. Technical Advisory Group for ISO TC 197 and Permanent Editing Committee.

**TC 4** - The NHA will participate in safety conference calls with other organizations, including the U.S. Fuel Cell Council.

**CSW 1** – The NHA will plan and conduct a hydrogen safety codes and standards workshop to advance NHA Codes and Standards work items. NHA will prepare and distribute a report on the workshop. Scheduled for late September 2001.

**TC 5** – The NHA will attend scheduled meetings of the ICC Ad hoc Hydrogen Committee and review available materials.

#### **FY02: Continuation of WHEC, ICC, ISO and NHA C&S efforts**

**CSW 2** - The NHA will plan and conduct a workshop to advance the NHA Codes and Standards work items. NHA will prepare and distribute a report on the workshop. Scheduled for March 2002.

**TC 6** - Staff will participate in the DOE Fuel Cell Codes and Standards Summit.

**TC 3** - The NHA will participate in hydrogen safety activities related with the World Hydrogen Energy Conference, including the ISO TC 197 Plenary and working group meetings.

**TC 7** - Staff will attend the 2002 Fuel Cell Summit and apply to present a poster on the safety codes and standards activities.

**TC 8** - Staff will participate in the DOE Hydrogen Program Peer Review.



**Hydrogen Codes and Standards Outreach  
National Hydrogen Association**

Task Designation/Milestone		FY2002					2003
		Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4	Qtr 1
TC1	◆						
TC2	◆						
TC3		◆					
TC4	◆			◆			
TC5	◆		◆			◆	
TC6			◆				
TC7					◆		
TC8					◆		
CSW1	★						
CSW2				★			

FY2002 Begins October 1, 2001

★ = Critical Milestone

◆ = Milestone

## 4.0 STATUS and PLANS

### 4.1 National Recognition

As the Hydrogen Program has grown in size over the past several years, so has it grown in stature as seen by the year-to-year increase in the number of patents, patent applications, awards, and other forms of recognition of achievement. These merits are itemized in this section.

#### FY 1994

P. Weaver, and P. -C. Maness (NREL), "Photoconversion of Gasified Organic Materials into Biologically Degradable Plastics," U.S. Patent 5, 250,427, issued October 5, 1993.

Dr. P.F. Weaver and his NREL research group also have a patent pending entitled, "Photoconversion of Gasified Organic Materials into Single-Cell Protein."

C. Linkous (FSEC), "Apparatus and Method for the Electrolysis of Water Employing a Sulfonated Solid Polymer Electrolyte," U.S. Patent 5,271,813, issued December 21, 1993.

Dr. Linkous (FSEC) also received the 1994 Distinguished Researcher Award from the University of Central Florida Centers and Institutes.

#### FY 1995

Midwest Research Institute's *President's Award* was presented to Dr. John Turner (NREL) for exceptional performance, 1995.

Dr. Eli Greenbaum of ORNL received the 1995 DOE Biological and Chemical Technologies Research Program Technical Achievement Award.

M.J. Antal (University of Hawaii), Catalytic Supercritical Gasification of Wet Biomass, U.S. Patent Application; Serial No. 08/414,523.

J. Woodward, S. Mattingly, and M. Danson (Oak Ridge National Laboratory), patent application: "An Enzymatic Process for the Generation of Molecular Hydrogen from Glucose".

D. Benson (National Renewable Energy Laboratory), invention disclosure: Disclosure to NREL patent office on new design for chemochromic hydrogen detector.

Sandia National Laboratories - 3 patent disclosures:

- G. Thomas, "Metal alloy for hydrogen storage,"
- G. Thomas, "Process for manufacturing hydride beds," and
- G. Thomas, "Synthesis of magnesium alloys with controlled phase."

K. Sapru et al (Energy Conversion Devices, Incorporated), patent application: "Magnesium Mechanical Alloys for the Thermal Hydrogen Storage," Patent application serial number 08/363,205, filed 22 Dec. 1994.

**FY 1996**

Dr. M.J. Heben (NREL) was invited to perform research in solar production of carbon nanotubes in France at The Universite Montpellier II by the French Ministry of Foreign Affairs.

M. L. Ghirardi and M. Seibert (NREL) filed a Record of Invention Report (NREL No. 96-46) entitled "A Technique Based on H<sub>2</sub>-Production Pressure to Select for Algal Mutants that Produce Hydrogen Under Aerobic Conditions", July 1996.

Dr. P.F. Weaver (NREL) filed a U.S. patent application entitled "Photoconversion of Thermally Gasified Biomass into Single-cell Protein."

Dr. Jonathan Woodward (ORNL) applied for a patent entitled "Enzymatic Method for Hydrogen Production from Glucose. U.S. patent application, esid-1833-x.

Dr. David Benson (NREL) filed a patent application "Fiber Optic Sensing Device" (May 1996).

Dr. Benson (NREL) was also recognized by the Hydrogen Technical Advisory Panel for "Ingenuity and Research Excellence in development of the fiber optic hydrogen sensor" (April 1996).

Drs. C. Jensen and W.C. Kaska (University of Hawaii), A U.S. Patent was awarded entitled "Process for Alkane Dehydrogenation with Organometallic Catalyst," U.S. Patent 5,687,717.

Members of the Air Products and Chemicals, Inc. SER group have two patents pending:

- Nataraj, S.N., Carvill, B.T., Hufton, J.R., Mayorga, S.M., Gaffney, T.R., and Brzozowski, J.R., "Process for Operating Equilibrium Controlled Reactions," U.S. Patent Pending (1996).
- Mayorga, S. G., Golden, T. C., Gaffney, T. R., Brzozowski, J. R., and Taylor, F. W., "Carbon Dioxide Pressure Swing Adsorption Process Using Modified Alumina Adsorbents," U. S. Patent Pending (1996).

C. Zawodzinski and M.S. Wilson (LANL), submitted a Formal Disclosure to the LANL Patent Office entitled "Stainless Steel Wire Mesh Flow Fields for Polymer Electrolyte Fuel Cells", November 1995.

The following recognition was afforded SERC's Palm Desert Project:

- The British Broadcasting Corporation's crew visited SERC and produced a clip that appeared during May 1996 on the BBC's show, *Tomorrow's World*.
- Newspaper and magazine articles: SERC's project was mentioned in numerous local, regional, national, and international newspapers. In addition, the December 1995 *Scientific American* ran an article about the Palm Desert Project.
- Demonstrations: Demonstrations of SERC's fuel cell powered PUV were conducted for the President of the AAA (American Automobile Association), commissioners of the CEC (California Energy Commission), the Chairman of the Board of CARB (the California Air Resources Board), at the Sacramento Municipal Utility District's Clean Power Day, at the Los Angeles Fleet Auto Show/Eco Expo, and at the City of Palm Desert's Clean Power Day.

Dr. Clovis Linkous (FSEC) was awarded U.S. patent #5,518,992, for "Photocatalytic Surfacing Agents for Inhibiting Algae Growth," May 21, 1996.

SNL has filed a patent disclosure entitled: "Continuous Microcellular Interstitial Media as an Immobilization Matrix,"

Energy Conversion Devices, Incorporated have filed the following patent applications:

- K. Sapru et al. "Robust Metal Hydride Hydrogen Storage System," Patent application serial number 08/569,487, filed 08 Dec. 1995.
- K. Sapru et al. "Robust Metal Hydride Hydrogen Storage System with Metal Support Structure," Patent application serial number 08/623,497, filed 03 Mar. 1996.

Dr. J. Bellan was awarded the Exceptional Service Award for Technology and Applications Programs from the Jet Propulsion Laboratory. The inscription reads: "In recognition of exceptional contribution in multiphase and reactive flows and combustion phenomena that have wide range of application in propulsion and aircraft engine design".

### **FY1997**

Drs. M. L. Ghirardi and M. Seibert (NREL) filed a Patent Application on the invention entitled "A Technique Based on H<sub>2</sub>-Production Pressure to Select for Algal Mutants that Produce Hydrogen Under Aerobic Conditions", April 1997.

Dr. Michael Seibert (NREL) received an NIS-IPP grant to work with a Russian group on a project that will support the Hydrogen Program's biohydrogen efforts.

Dr. Seibert (NREL) received an invitation from a Spanish Laboratory to give a seminar with travel expenses paid by the Spanish government.

Dr. Seibert's group (NREL) received a request from a Swiss National Laboratory to join the group as a postdoctoral fellow at the expense of the Swiss government.

Dr. John Turner (NREL) and Dr. Rick Rocheleau (U Hawaii) were co-recipients of the HTAP second annual Hydrogen Program Research Success Story Award for work on "Photoelectrochemical Systems for the Production of Hydrogen".

Dr. David Benson (NREL), who had a patent application for his Hydrogen sensor in the FY 1996 listings, has also applied for an international patent. The patent application was issued in October 1997 as International Publication Number WO 97/37258. This is the first step in the process of obtaining international patents. Designated countries include Belgium, Switzerland, Denmark, Finland, Great Britain, Italy, Netherlands, Austria, Ireland, Spain, Australia, France, Luxembourg, Monaco, Portugal, Germany, Greece, Australia, Japan, and Canada.

Dr. George Thomas (SNL) has filed a patent disclosure concerning an immobilization method for a hydride bed.

Dr. Craig Jensen and his associates at the University of Hawaii have filed the following two patent applications on polyhydride storage complexes:

"Low Temperature Catalytic System for Chemical Storage of Hydrogen" Craig M. Jensen; U.S. Patent 8,807,123 filed February 1997.

Dr. Clovis Linkous of FSEC was awarded the Orlando Section of the American Chemical Society's "Outstanding Chemist Award in December 1996

The SERC/Palm Desert Project has gained additional exposure to that which was reported in FY 1996: Articles about the project have appeared in:

- *Popular Science* (September 1996, October 1996)
- *Motorland Magazine* -a publication of the American Automobile Association (Nov/Dec 1996)
- *Wired Magazine* (October 1997)
- A video about the project has appeared on *Understanding Cars*, The Learning Channel, May, 1997

Oak Ridge National Laboratory Awards Night, "Technical Achievement Award, Invention" May 1997 to B. S. Hoffheins, R. J. Lauf, and P. H. Fleming.

F. Mitlitsky, B. Myers, and F. Magnotta, LLNL have filed an invention disclosure, "Lightweight bladder lined pressure vessels." *Disclosure and Record of Invention*, DOE Case No. IL-9722 (1995).

The Savannah River Bus Project was awarded the Federal Laboratory Consortium "1996 Southeast Regional Partnership Award"

Personnel involved with the Savannah River Bus Project were awarded the "Keys to City of Augusta", by Mayor Larry Sconyers and Senator Sam Nunn (D-GA).

C. Zawodzinski and M.S. Wilson, of the LANL PEM Fuel Cell Team have submitted a patent application to the US Patent Office entitled "Stainless Steel Wire Mesh Flow Fields for Polymer Electrolyte Fuel Cells."

Drs. J. Bellan and R. S. Miller were awarded NASA Certificates of Recognition (recognition for best and most important papers within NASA) were awarded for the following publications:

- "Analysis of Reaction Products and Conversion Time in the Pyrolysis of Cellulose and Wood Particles"
- "A Generalized Biomass Pyrolysis Model Based on Superimposed Cellulose, Hemicellulose and Lignin Kinetics"
- "Tar Yield and Collection from the Pyrolysis of Large Biomass Particles"

Dr. Jonathan Woodward (ORNL) was awarded the Columbus Award for his glucose to hydrogen work

## **FY 1998**

The ORNL Team won a Lockheed Martin Energy Research, Corp. invention award at the 1997 Awards Night.

Weaver, P.F., (NREL) "Photoconversion of Thermally Gasified Biomass into Single-cell Protein." U.S. Patent application filed and appeal defended.

A Notice of Allowance was received from the US Patent Office regarding M. L. Ghirardi and M. Seibert's (NREL) Patent "Process for Selecting Oxygen Tolerant Algal Mutants that Produce H<sub>2</sub> under Aerobic Conditions" in July 1998.

M. Seibert, T. Flynn and D. Benson (NREL), A Patent Application on an invention entitled "A Chemochromic Sensor for Rapid Biohydrogen Phenotypic Screening" was filed in May 1998.

David K. Benson, Clemens S. Bechinger and C. Edwin Tracy (NREL), Fiber Optic Device for Sensing the Presence of a Gas, US Patent No. 5,708,735, January 13, 1998.

NREL filed a provisional patent application on a closely related hydrogen sensor that is being successfully used by NREL bio-hydrogen researchers to facilitate the selection of hydrogen-producing mutant algae.

M.S. Wilson and C. Zawodzinski (LANL), "Stainless Steel Wire Mesh Flow-Fields for Polymer Electrolyte Fuel Cells," Patent issued by the US Patent Office (No 5798187, Aug 25, 1998).

F. Mitlitsky, B. Myers, and F. Magnotta (LLNL), "Lightweight bladder lined pressure vessels" *Disclosure and Record of Invention*, DOE Case No. IL-9722, U.S. Patent No. 5,798,156, August 25 (1998).

F. Mitlitsky, J.B. Truher, J.L. Kaschmitter, and N.J. Colella (LLNL), "Fabrication of polycrystalline thin films by pulsed laser processing", *Disclosure and Record of Invention*, DOE Case No. IL-9123, U.S. Patent No. 5,714,404, February 3 (1998).

M.J. Antal, (U Hawaii), Catalytic Supercritical Gasification of Wet Biomass, U.S. Patent Application; Serial No. 08/414,523.

M.J. Antal, X. Xu (U Hawaii), Catalytic Supercritical Gasification of Biomass Starch Pastes, U.S. Provisional Patent Application.

Craig M. Jensen, and William C. Kaska (U Hawaii) Patent 5,780,701 Process for Alkane and Alkyl Group Dehydrogenation with Organometallic Catalyst; Issued 7/98.

Sandia National Laboratories Patent Disclosures and Status:

- Bed Immobilization Method – nearing completion
- Mg alloy – re-submitted

The Hydrogen Technical Advisory Panel (HTAP) awarded the Safety Analysis work at the University of Miami their Research Excellence Award on March 3, 1998 at the 9<sup>th</sup> Annual US Hydrogen Meeting.

Savannah River Technology Center: Invention disclosure filed for membrane separation system.

ECD - Two patent applications filed:

- "Metal Hydride Storage Container with Valved Ports", filed 1/20/98
- "Self-Heating Metal Hydride Hydrogen Storage System," filed 2/13/98.

## **FY 1999**

Massachusetts Institute of Technology:

- *Plasma Fuel Converter using High Voltage, Low Current Operation*, US patent Office application, 1999
- *Low Power Compact Plasmatron Fuel Converter*, US patent application (continuation-in-part of the above application), 1999

- MIT Paper presented at the Fall Meeting of the American Chemical Society was nominated for the Glen Award.

M. Seibert, D.K. Benson and T.M. Flynn (NREL), a patent entitled "A Chemochromic Sensor for Rapid Biohydrogen Phenotypic Screening" was filed, May 1999.

Weaver, P.F. (NREL) "Photoconversion of Thermally Gasified Biomass into Single-cell Protein." U.S. patent application filed and appeal defended.

Dr. James Weifu Lee (ORNL) received two awards in FY 1999:

- DOE Early Career Award for Scientists and Engineers
- Presidential Early Career Award for Scientists and Engineers.

Dr. Lee was honored in ceremonies at DOE headquarters and the Old Executive Office Building. The awards were presented by Secretary of Energy Bill Richardson and Presidential Science Advisor Neal Lane.

R. J. Lauf, (ORNL), A patent application for "Resistive Hydrogen Sensing Element" was filed May 10, 1999.

Dr. Peter Van Blarigan (SNL), a patent application was filed for "Free Piston Engine".

Peter Van Blarigan, Sandia National Laboratory 1998 Harry Lee Van Horning Memorial Award. This was awarded by an SAE board of award in October 1999 for the single most outstanding technical contribution to SAE for 1998 in the fields of engines, fuels and combustion.

Savannah River Technology Center: Patent was awarded on composite metal hydride materials.

M.J. Antal (U of Hawaii) Catalytic Supercritical Gasification of Wet Biomass, U.S. Patent Application; Serial No. 08/414,523.

1999 Research Success Story Award, presented to Craig M. Jensen (U Hawaii) by the US Department of Energy Hydrogen Program Technical Advisory Panel, April 6, 1999.

Craig M. Jensen and Ragaiy A. Zidan (U Hawaii) "Novel Hydrogen Storage Materials and Method of Making by Dry Homogenation (provisional patent filed 8/98); (full patent filed, 5/99).

M. S. Wilson (LANL) "Fuel Cell Membrane Humidification," US Patent No. 5,952,119. Sept. 14, 1999.

Sapru, Krishna; Ming, Lu; Ramachandran, Subramanian, (ECD) US Patent Number 5916381 "Magnesium Mechanical Alloys for Thermal Storage" Aug 29, 1999

J. Woodward, and S.M. Mattingly, (ORNL) "Method for the Enzymatic Production of Hydrogen" U.S. Patent 5,942,424 Aug 24, 1999.

A provisional patent application entitled "Hydrogen Production Using Hydrogenase-Containing Oxygenic Photosynthetic Organisms" by A. Melis, L. Zhang, J.R. Benemann, M. Forestier, M. Ghirardi and M. Seibert (U California, Berkeley and NREL) was filed on Dec. 28, 1999.

**FY 2000**

S. Nataraj, R.B. Moore and S.L. Russek, (Air Products and Chemicals) U.S. Patent 6048472, April 2000, "Production of Synthesis Gas by Mixed Conducting Membranes".

S. Nataraj and S.L. Russek, (Air Products and Chemicals) U.S. Patent 6077323, June 2000, "Synthesis Gas Production by Ion Transport Membranes".

S. Nataraj and S.L. Russek, (Air Products and Chemicals) U.S. Patent 6110979, August 2000, "Utilization of Synthesis Gas Produced by Mixed Conducting Membranes".

S. Nataraj, P.N. Dyer, and S.L. Russek (Air Products and Chemicals) U.S. Patent 6114400, September 2000, "Syngas Production by Mixed Conducting Membranes with Integrated Conversion into Liquid Products".

M. S. Wilson and C. Zawodzinski (LANL) "Fuel Cell with Metal Screen Flow-Field," US Patent No. 6,037,072. March 14, 2000.

A. Q. Pham, P. H. Wallman, and R. S. Glass, (LLNL) "Natural Gas-Assisted Steam Electrolyzer," U. S. Patent No. 6,051,125 (April 18, 2000).

Peter Van Blarigan, (SNL), "Free Piston Engine" –pending 2000 – claims accepted.

Sapru, K. (ECD) "Magnesium Mechanical Alloys for Thermal Hydrogen Storage" US Patent No. 6,103,024, August 15, 2000

Sapru, K. (ECD) "Self-Heating Metal-Hydride Hydrogen Storage System" US Patent No. 6,099,811, August 8, 2000

Sapru, K. (ECD) "Magnesium Mechanical Alloys For Thermal Hydrogen Storage" US Patent Number 5,976,276, November 2, 1999

Bhandari and Baum (ATMI), "Hydrogen Sensor Utilizing Rare Earth Metal Thin Film Detection Element", US Patent Number 6,006,582, December 1999.

Craig M. Jensen (U Hawaii), "Hydrogen Storage" US patent # 6,074,447; issued 6/13/00.

N. Muradov (FSEC), "Thermocatalytic Process for CO<sub>2</sub>-free Production of Hydrogen and Carbon from Hydrocarbon Fuels", U.S. Patent Application, No. 60/194828, filed 04/05/2000

N. Muradov (FSEC), "Portable Hydrogen Generator", U.S. Patent Application, No. 60/203370, filed 05/10/2000

NREL Record of Invention IR 00-34, "Solar Thermal Aerosol Flow Reaction Process, "Alan Weimer, Jaimee Dahl, Joseph Tamburini, Allan Lewandowski, J. Roland Pitts, Carl Bingham NREL and U Colorado) UTC File No. 10058; SN 60/203, 186. Submitted as a provisional patent to the U.S. Patent Office, May 8, 2000.

The 2000 HTAP Research Success Story Award was presented to M.J. Heben for NREL's work in hydrogen storage using carbon nanotubes.



A.C. Dillon, T. Gennett, and M.J. Heben, (NREL), ROI #99-22 "Pure Single-Wall Carbon Nanotubes", was converted into a full Patent Application on 8/10/00.

A.C. Dillon, T. Gennett, J.L. and M.J. Heben (NREL) ROI #99-44 "Cutting of Single-Wall Carbon Nanotubes for Hydrogen Storage or Superbundle Formation", was filed as a Provisional Patent Application on 1/19/00.

A.C. Dillon, T. Gennett, J.L. and M.J. Heben. (NREL) ROI #00-44 "Single-Wall Carbon Nanotubes for Metal-Hydride Assisted Hydrogen Storage or Superbundle Formation", was filed on 7/7/00:

Weaver, P.F. (NREL) "Photoconversion of Organic Materials into Single-cell Protein." U.S. patent allowed NREL IR Number 90-40FWC, serial number 07/959,519.

M. Seibert (NREL) was elected Fellow of the American Association for the Advancement of Science.

SunLine Transit Agency won the 1999 Governor's Environmental and Economic Leadership Award.

Sandia National Laboratory:

- Patent No. 5,866,623 awarded – Method for immobilizing particulate material in packed beds.
- Patent No. 5, 895,518 awarded – Synthesis of alloys with controlled phase structure.
- New disclosure submitted on bed assembly, G. Cook Story and R. Baldonado.

## **FY 2001**

Alan Weimer, Jaimee Dahl, Joseph Tamburini, Allan Lewandowski, J. Roland Pitts, Carl Bingham (NREL and U Colorado) NREL Record of Invention IR 00-34, "Solar Thermal Aerosol Flow Reaction Process," UTC File No. 10058; SN 60/203, 186, submitted as a provisional patent to the U.S. Patent Office, May 8, 2000.

Irving, Patricia (Innovatek), U.S. Provisional Patent Application No. 60/305,389. Hydrocarbon Fuel Reforming Catalyst And Use Thereof, Filed July 13, 2001.

S. Nataraj and S.L. Russek (ACPI), "Synthesis Gas Production by Ion Transport Membranes", US Patent 6,214,066, April 2001.

Jet Propulsion Laboratory, California Institute of Technology – 3 NASA Certificates of Recognition, as follows:

- Model of Fluidized Bed Containing Reacting Solids and Gases
- Numerical Study of Pyrolysis of Biomass in Fluidized Beds
- Assessment of Models of Chemically Reacting Granular Flows

An Intellectual Property Disclosure on continuous-flow biohydrogen reactor was filed to the Iowa State University Office of Intellectual Property and Technology Transfer in March 2001. A US Patent application is in progress.

Weaver, P. F. (NREL) "Photoconversion of Fuel Gases into Single-Cell Protein", U.S. Patent #6,187,565 B1 issued Feb. 13, 2001.

Westinghouse Savannah River Technology Center, "Container and method for absorbing and reducing hydrogen concentration", U.S. patent 6,262,328 issued July 17, 2001.

C.A. Linkous and N.Z. Muradov (FSEC), "Closed Cycle Photocatalytic Process for Decomposition of Hydrogen Sulfide to its Constituent Elements," U.S. patent #6,248,218, June 19, 2001.

M. Seibert, T. Flynn and D. Benson (NREL), "Apparatus for Rapid Biohydrogen Phenotypic Screening of Microorganisms using a Chemochromic Sensor", Utility Patent Application (May 2000).

A. Melis, L. Zhang, J. R. Benemann, M. Forestier, M. Ghirardi and M. Seibert (NREL), "Hydrogen Production using Hydrogenase-containing oxygenic Photosynthetic Organisms", Utility Patent Application (Dec. 2000).

A.C. Dillon, T. Gennett, J.L. and M.J. Heben (NREL), Patent application: "Single-Wall Carbon Nanotubes for Metal-Hydride Assisted Hydrogen Storage or Superbundle Formation".

L. Grigorian, G.L. Hornyak, A.C. Dillon and M.J. Heben (NREL), Patent application: "Chemical vapor growth of SWNTS".

Westinghouse Savannah river Technology Center, Invention Disclosure: "New Method for Making Doped Nanotubes".

SNL, Patent No. 5,866,623 awarded – "Method for immobilizing particulate material in packed beds".

SNL, Patent No. 5,895,518 awarded – "Synthesis of alloys with controlled phase structure".

Peterson Ridge, LLC, Patent application Serial No. 60/192,807.

SNL, "Free-Piston Engine" – U.S. Patent No. 6,199,519 issued March 13, 2001.

Steve W. Martin, Renaud Belin, Jacob Sutherland (Iowa State University), "New Glass-Ceramic Proton Conducting Solid Electrolytes," ROI ISURF 02840, July 5, 2001.

Bhandari and Baum (ATMI), "Hydrogen sensor utilizing rare earth metal thin film detection element", US Pat. 6,006,582, December 1999.

DiMeo and Bhandari (ATMI), "Micro-Machined Thin Film Hydrogen Gas Sensor, and Method of Making and Using the Same", U.S. Patent No. 6,265,222, July 2001.

SunLine, Southern California Emergency Services Association (SCESA) Public Sector Silver Award.

SunLine, American Public Transit Association's AdWheel Award (small transit system group) for annual report.

SunLine, California Transit Association Small Operators Committee Transit Innovation Award.

SunLine, American Public Transit Association Certificate of Achievement in Recognition of Outstanding Safety Achievements in Bus Service 2000 (1 of 100 finalists for the Gold Award).

SunLine, *Natural Gas Fuels* Magazine "Best NGV Fleet Operation, Public Sector" in third annual Reader's Poll.

QUANTUM received the WestStart 5<sup>th</sup> Annual Blue Sky Merit Award. WestStart -the advanced transportation consortium - to recognize the outstanding contributions of companies that bring clean-fuel

vehicles to market and help to increase the awareness of their need presents the award each year, March 2001.

The Hydrogen Technical Advisory Panel's Technology Innovation Award (HTAP) was granted to Lawrence Livermore National Laboratories for work with QUANTUM and Thiokol in achieving the September 2000 breakthrough in advanced hydrogen storage (mass performance record of 11.3% hydrogen storage by weight @ 5,000 psig), May 2001.

## 4.2 FY 2001 Major Accomplishments

### 4.2.1 Production

#### Thermal Dissociation of Methane Using a Solar-Coupled Aerosol Flow Reactor – NREL

- Preliminary experiments for methane dissociation were encouraging with the indicated degree of dissociation being consistent with measured temperatures and gas flow rates.
- A math model of the Thagard electrically heated graphite reactor process (U.S. Patent 4,095,974) has allowed the reaction kinetics for natural gas dissociation at high temperatures and in the presence of flowing carbon black particles to be determined. This kinetics rate expression will be used in the eventual solar-thermal reactor model.

#### Production of H<sub>2</sub> by Superadiabatic Decomposition of Hydrogen Sulfide - Gas Technology Institute (GTI)

- Developed a mathematical method to estimate hydrogen production by superadiabatic decomposition of H<sub>2</sub>S
- Demonstrated theoretical feasibility of hydrogen production over a wide range of operating conditions
- Designed a lab-scale testing system to collect the necessary experimental data to demonstrate the technical feasibility of the process

#### Thermocatalytic CO<sub>2</sub>-free Production of Hydrogen from Hydrocarbon Fuels - Florida Solar Energy Center (FSEC)

- Found methane decomposition rate was highly accelerated by the presence of unsaturated and aromatic hydrocarbons and was inversely proportional to carbon crystallite size.
- Selected a fluidized bed reactor as the most suitable reactor for the continuous methane decomposition process.
- Designed, fabricated and tested a 1 kW thermocatalytic reactor for CO/CO<sub>2</sub>-free production of hydrogen and carbon using propane and methane as feedstocks. The concentration of hydrogen in the propane pyrolysis gas reached up to 80-85 v.%, with the balance being methane.
- Connected 1 kW thermocatalytic reactor to a PEM fuel cell and tested using methane and propane as fuels.
- Techno-economic evaluation of thermocatalytic production of hydrogen and carbon from natural gas conducted in cooperation with NREL.

#### Novel Catalytic Fuel Reforming – InnovaTek, Inc.

- Developed and tested proprietary non-coking, sulfur tolerant catalyst in a continuous 150-hr natural gas steam reforming run.
- Successfully integrated the steam reformer with an H-separation membrane in an initial experiment with methane. Almost 700 cc/minute of pure hydrogen was obtained from the membrane. The reaction efficiency was 81% and the membrane recovery was 70%.

### Engineering Development of Ceramic Membrane Reactor Systems for Converting Natural Gas to Hydrogen and Synthesis Gas for Liquid Transportation Fuels – Air Products and Chemicals, Inc.

- Norsk Hydro completed an evaluation of ITM H<sub>2</sub> for large hydrogen plants producing 760 million SCFD of fuel grade H<sub>2</sub>, with capture of CO<sub>2</sub>. The capital cost of a greenfield ITM H<sub>2</sub> process was found to be up to 15% lower than an oxygen-blown ATR process with an Air Separation Unit; and up to 22% lower for Inside Battery Limit scope.
- Eltron Research demonstrated the achievement of the design oxygen flux at 850°C to 950°C for up to 600 hours.
- Tests at Eltron Research demonstrated the performance of ceramic membranes and seals at 250 psig and over 800 °C for over six months, with good oxygen flux stability.
- McDermott performed finite element analysis of the PDU membrane using simplified material and thermal profile assumptions to assess different design details. Structural analysis was also performed in support of the design of the PDU module. A computational fluid dynamics analysis was performed to assess flow distribution in the PDU.
- Completed construction on the ITM Syngas PDU. Nominal capacity: 24,000 SCFD of syngas throughput.

### Integrated Ceramic Membrane System for Hydrogen Production – Praxair

- Found the efficiency of the integrated ceramic membrane system comparable to SMR (steam methane reforming) process.
- Determined that meeting DOE goal (\$8/MMBtu) will require lower capital costs as well as high capacity utilization.

### Fluidizable Catalysts for Hydrogen Production from Biomass Pyrolysis/Steam Reforming – National Renewable Energy Laboratory

- Identified a fluidizable catalyst support that could withstand reforming conditions for extended operation. Catalysts made with this support were tested under actual reaction conditions.

### Biomass Pyrolysis for Hydrogen Production – Jet Propulsion Laboratory

- Found that the most important parameter determining the tar yield in a fluidized bed reactor is the fluidizing gas temperature. Biomass particle size also has a major influence on the tar yield.

### Supercritical Water Partial Oxidation – General Atomics

- Completed configuration of the GA-owned supercritical water test facility for SWPO operation was completed including design, procurement and integration of a high-pressure oxygen system. The SWPO test system was checked out, debugged and systemization runs successfully completed.
- Demonstrated the ability to develop significant quantities of hydrogen during first cornstarch test series in down-flow reactor. Observed hydrogen yield on the order of 150% of input (feed-based) hydrogen implying significant contribution from shift reactions.

Biohydrogen Production from Renewable Organic Wastes – Iowa State University

- Studied the effect of pH (4.5 to 7.5) and substrate concentration (1.5 to 44.8 g COD / L) and their interaction on biohydrogen production. Highest conversion efficiency of 30% based on COD with hydrogen content of 55 - 82% was achieved.
- Found that batch sequential batch feeding is better suited to hydrogen production as seen from the hydrogen yields. Batch feeding can flush out dilute sporulation promoting substances, which further enhance hydrogen production.

Bio-production of Hydrogen using Thermophilic Bacteria – NETL

- Determined that 4-12% oxygen gas in the headspace at the start of the batch experiment is crucial to obtaining high hydrogen production.
- Found that oxygen is actively utilized in the hydrogen generation process. In the absence of sufficient oxygen, only low levels of hydrogen are produced.

Hydrogen from Post-consumer Wastes – NREL

- Catalyst tests identified that high temperature steam was the main factor that contributed to the catalyst losses. A 100-hour-long room-temperature attrition test using nitrogen as the fluidizing gas showed catalyst losses of 2%. The losses during a 50-hour-long steam reforming of methanol (thermal stress, no coke formation) were 9%. Finally, a 120-hour-long reforming of natural gas and pyrolysis liquid resulted in the catalyst losses of 26%, comparable with those for processing methanol.
- Demonstrated process flexibility by reforming trap grease, a low-cost feedstock of high potential for producing hydrogen, and co-reforming carbohydrate-derived fraction of bio-oil and natural gas. Very encouraging results were obtained for both cases.

Biological Hydrogen from Fuel Gases and from Water – NREL

- Developed a kinetic H-D exchange assay to continuously monitor hydrogenase activity with the simultaneous presence of O<sub>2</sub> using a capillary mass spectrometer. Determined that the bacterial hydrogenase is functional even in the presence of 3% O<sub>2</sub>, with the activity proceeding at a linear rate for the duration of the 10-min assay.
- Continued to develop various selection/enrichment techniques to generate mutants either deficient in or enhanced in the CO shift activity. Based on their requirement for CO<sub>2</sub> in order for photosynthetic bacteria to utilize acetate as a carbon substrate, derived seven variants that exhibit elevated levels of CO shift activity.

Bioreactor Development For Biological H<sub>2</sub> Production – NREL

- Successfully operated both 1-L and 5-L bioshift reactors in the laboratory. Demonstrated the successful prediction of the performance of the larger reactor based on the performance of the smaller reactor.
- Successfully operated a bioshift reactor on a slipstream of biomass-derived synthesis gas from the NREL Thermochemical User Facility. Found no decrease in bioshift activity despite the presence of both toluene and benzene at concentrations exceeding 2000 ppmv in the water-scrubbed synthesis gas over the course of the four-day experiment.

Separation Membrane Development - Westinghouse Savannah River Technology Center

- Produced hundred-gram size sample from small batches, but consistent results require close control of parameters.
- Found that a small U-shape column in combination with an open-top furnace is an ideal setup for studying temperature swing absorption.

Defect-Free Thin Film Membranes for H<sub>2</sub> Separation and Isolation – Sandia National Laboratories

- Synthesized and permeation tested defect-free ZSM-5 aluminosilicate zeolite films. These are 2-sided membranes
- Showed aluminosilicate films to have **superior** flux and separations of H<sub>2</sub> versus CH<sub>4</sub>, CO<sub>2</sub>, O<sub>2</sub> and N<sub>2</sub>.

Solar Photocatalytic Hydrogen Production from Water Using a Dual Bed Photosystem - Florida Solar Energy Center

- Found that cyanine and merocyanine dyes were not stable enough in aqueous alkaline systems to be used as photocatalysts.
- Found that the use of irreversible reducing agents such as EDTA did not substantially increase the hydrogen gas evolution rates. That would imply the rate-determining step is a solid state effect inside the organic photocatalyst.

Photoelectrochemical Based Direct Conversion Systems For Hydrogen Production - NREL

- Showed that in triple junction silicon samples a-SiC offers some protection, but reduces the efficiency due to a resistive interface.
- Showed for the first time that it is possible to move the band edges of a semiconductor from a position where water splitting is impossible, to a position where water splitting might be possible. This was accomplished by modifying Gallium Indium phosphide with a ruthenium porphyrin, resulting in a shift in the band edges of almost 0.5 volts. This is sufficient to allow the band edges to overlap the water redox potentials.

Photoelectrochemical Hydrogen Production – University of Hawaii, Manoa

- Developed sputtered NiMo films with lower overpotential as lower-cost alternative to CoMo films previously used as HER catalyst.
- Developed triple junction a-Si cells on metal substrates with electrical efficiencies up to 12.7%. (University of Toledo sub-contract)
- Completed small-scale hydrogen photoreactor with gas collection and solar-tracking.
- Developed new hybrid photoelectrode design developed with photoactive active outer layer to enhance photoelectrode performance and stability.

Maximizing Photosynthetic Efficiencies and Hydrogen Production in Microalgal Cultures – University of California Berkeley

- Identified three *Chlamydomonas* mutants with a **truncated Chl antenna size** and further identified some of the corresponding genes that are involved in this process. The *tha1* transformant has the smallest Chl antenna size of all mutants currently at hand, being about half the size of the wildtype.
- Found that the absence of lutein affects the functional Chl antenna size of PSII but not that of PSI. A lesion in the *lycopene  $\epsilon$ -cyclase* gene prevents synthesis of lutein and affects the Chl antenna size of photosynthesis. Xanthophyll-biosynthesis genes may be targets for a truncated Chl antenna size.

Molecular Engineering of Algal H<sub>2</sub> Production – NREL

- Cloned a fragment of the algal reversible hydrogenase by RT-PCR, using primers designed to hybridize to the H-cluster of other known Fe-only hydrogenases. The fragment was used to screen a cDNA library that yielded the full clone (HydA).
- Cloned a second hydrogenase gene following the discovery of an EST in Genbank with high degree of homology to the active site of Fe-only hydrogenases. This yielded a transcript, HydB, of the same size as HydA. The second hydrogenase is different from HydA both at the nucleotide and amino acid level. Northern blots have shown that the two hydrogenases are expressed similarly upon anaerobic induction.

Cyclic Photobiological Algal H<sub>2</sub>-Production – NREL

- Found that depletion of ions other than sulfur from the growth medium also selectively inactivates O<sub>2</sub> evolution. However, the rate of inactivation is lower than that obtained by sulfur depletion.
- Found that specific inhibitors of Photosystem II-mediated O<sub>2</sub> evolution inhibit H<sub>2</sub> production by about 80%.

International Energy Agency and Other International Collaborations – NREL

- Defined the program of work for the Biomass to Hydrogen Subtask of the proposed Task on Hydrogen from Carbon Containing Materials.
- Attended two Executive Committee and ten Experts meetings. The Executive Committee meetings focused on expanding the membership in the Hydrogen Agreement and launching new task efforts. China, Denmark, Hungary, Israel, Mexico and the United Kingdom have received invitations to join the IEA activities.
- Completed two life cycle assessments in support of the IEA Integrated Systems Task. The first was on a remote application for Norway that involved wind electrolysis to produce hydrogen to fuel a public transit bus. The second scenario assessed hydrogen options for residential heat and electricity in the Netherlands.
- Drafted two state-of-the-art reports in support of the proposed IEA Task on Hydrogen from Carbon Containing Materials. The first was commissioned from Princeton University (Joan Ogden) and covered small-scale reformer technology for hydrogen production. The second was commissioned from Thomas A. Milne, with support from NREL personnel, and was on hydrogen production routes from biomass.
- Published the final report for IEA Task 12, Metal Hydrides and Carbon for Hydrogen Storage. It included a project report for the NREL-led activity on single-wall carbon nanotubes.



### Efficient Hydrogen Production Using Enzymes of the Pentose Phosphate Cycle - Oak Ridge National Laboratory

- Found that 6PGDH is the rate-limiting enzyme in the *in vitro* pathway as shown by the decrease in H<sub>2</sub> and CO<sub>2</sub> production on increasing the concentration of 6-phosphogluconic acid. This observation was confirmed by obtaining greater yields and rates of H<sub>2</sub> and CO<sub>2</sub> production on introducing more of the 6PGDH enzyme to the system.
- Cloned the genes encoding the enzymes of the oxidative branch of the pentose phosphate cycle (G6PDH and 6PGDH) from the hyperthermophile *Thermotoga maritime*. They are expressed in *Escherichia coli*.

### 4.2.2 Storage

#### Carbon Nanotube Materials for Hydrogen Storage - NREL

- Began producing SWNTs with a new industrial Alexandrite laser that is very robust. Multi-colored Raman measurements showed that the new laser produced SWNTs of differing diameters and chiralities. When the diameter and chirality distribution which was similar to that of the materials made by the previously-employed Nd:YAG laser was reproduced high hydrogen adsorption capacities was observed.
- A recent techno-economic analysis performed by Tim Eggeman of Neoterics International under a subcontract from NREL indicated that NREL/Honda joint intellectual property could lead to the production of SWNTs for prices in the range of \$1/kg.

#### Doped Carbon Nanotubes for Hydrogen Storage - Westinghouse Savannah River Technology Center

- Developed a new technique to produce large quantities of doped nanotubes

#### Catalytically Enhanced Hydrogen Storage Systems – University of Hawaii

- Showed that at the practically relevant conditions of 100 °C and a constant pressure of 1 atm, hydrogen is eliminated from NaAlH<sub>4</sub> doped with 2 mole percent titanium at the rate of 1.8 wt %/h which is adequate to meet the demands of an onboard fuel cell.
- Demonstrated that 50/50 mixtures of NaH and Al metal doped with 2 mole percent Zr(O<sup>n</sup>Pr)<sub>4</sub> were found to require less than 0.5 h to absorb >4 wt % hydrogen at 100 °C under 100 atm of hydrogen.
- Solid state <sup>1</sup>H NMR spectroscopy revealed that doping NaAlH<sub>4</sub> with titanium or zirconium results in a large increase in the proportion of mobile hydrogen in the **bulk** of the hydride.

#### Hydrogen Storage Development – Sandia National Laboratories

- Developed a new direct synthesis method for catalyzed NaAlH<sub>4</sub>. It provides the highest storage capacity and hydrogen absorption and desorption kinetics an order of magnitude faster than earlier materials.

Vehicular Hydrogen Storage Using Advanced Tanks – Lawrence Livermore National Laboratory

- Found that a factor of two cost reduction beyond the best projected economic performance of the best (type IV) current hydrogen vehicular tankage technology is available in mass production by the substitution of several manufacturing technologies (that have yet to be applied to compressed hydrogen tanks), combined with Statistical Process Research (of the sort done in semiconductor electronics, which has also yet to be performed on hydrogen tanks or other mass produced structures).
- Found that vehicle demonstration projects that might demonstrate advanced tankage or adequate range are no longer cost effective for the DOE Hydrogen Program due to liability issues.
- Determined that at least 325 1.25X EPA miles of vehicle range fit onto a SUV with already commercialized Type IV tank technology derived from LLNL liner and tank design innovations.

Advanced Thermal Hydrogen Compression – Ergenics, Inc.

- Demonstrated thermal hydrogen compressor operation to 6,000 psig, using a miniature hydride heat exchanger.
- Identified and tested a disproportionation-resistant hydride alloy suitable for extended compressor operation at high pressure and temperature.

**4.2.3 Utilization**Low Cost, High Efficiency, Reversible Fuel Cell Systems- Technology Management, Inc.

- Replicated reversible “round trip” efficiency (in single cells).
- Reduced operating temperature resulting in improved cell to cell performance variability.

Gallium Nitride Integrated Gas/Temperature Sensors for Fuel Cell System Monitoring for H<sub>2</sub> and CO – Peterson Ridge, LLC

- Confirmed the CO sensitivity between 50 and 500 ppm in 35% hydrogen (nitrogen balance) on GaN modulation-doping-semiconductor-field-effect-transistors (MODFETs) with Pt gate metal. The target detection limit for CO from various sources is 5 ppm with sensitivity to 100 ppm.

Internal Combustion Engines Research and Development - Sandia National Laboratories

- Found that uniflow scavenging allows approximately 85% of the exhaust gases to be scavenged out of the cylinder without significant short circuiting of fuel. Loop scavenging only allows 50% exhaust gas removal.

Reduced Turbine Emissions Using Hydrogen-Enriched Fuels - Sandia National Laboratory

- Found that the addition of to natural gas will extend the lean flammability limits allowing operation at lower flame temperatures and a significant reduction in NO<sub>x</sub> emissions.

Interfacial Stability of Thin Film Hydrogen Sensors - NREL

- Continued the study of failure mechanisms in thin film hydrogen sensors; there are distinct modes for different types of sensors. The primary mechanism responsible for a loss in performance over time with optical sensors is fouling of the hydrogen dissociation sites on the surface of the catalyst.
- Identified and tested protective layers for the Pd catalyst for periods as long as 3<sup>+</sup> months, with excellent results.
- Found methods for regenerating dead sensors. Sensors that have been dead for more than a year have been regenerated to almost pristine performance.

Integrated Micro-Machined Hydrogen Gas Sensor – Advanced Technology Materials, Inc. ATMI, Inc.

- Showed response levels of greater than 120% to 0.25% H<sub>2</sub> in dry air
- Measured response times of < 0.5 s
- Showed dynamic range of < 200 ppm H<sub>2</sub> to >1% H<sub>2</sub>
- Reduced power consumption of device design by >20%

Codes and Standards Analysis - University of Miami

- Present ventilation employed in the CaFCP building is adequate to reduce the risk of leaks up to 80 SCFM to that of a vertical column of hydrogen rising to the ceiling.
- Completed an experimentally verified CFD model of a 5,000 cubic foot warehouse
- Found that the presently used requirements for residential garage ventilation are not sufficient for hydrogen.
- A 5/8 inch sheet of Fire Code Type X gypsum board provided an order of magnitude better protection from a hydrogen flame than did a 0.060" sheet of cold rolled steel.

High Efficiency Steam Electrolyzer – Lawrence Livermore National Laboratory

- Improved the thin film coating process. With the improved process, the yield has improved from 20% to about 80% for tubes as long as six inches.
- Completed the tube characterization. The tubes, fabricated using cold isostatic pressing, can easily survive a pressure differential of 150 psi. Rapid temperature cycling appears to have no effect on the tube mechanical integrity.
- Completed the engineering design of the 200 W electrolyzer stack. A tube-to-tube series connection has been developed. This design approach enables the use of high voltage and low current. A metal-to-ceramic brazing technique has also been developed for the sealing of the tubes.

**4.2.4 Technology Validation**Engineering Scale Up of Renewable Hydrogen Production by Catalytic Steam Reforming of Peanut Shells Pyrolysis Products – NREL

- Designed, built, and installed the catalytic steam reformer reactor for biomass pyrolysis vapor reforming to hydrogen at NREL for shake down and initial testing.

Hydrogen Production Through Electrolysis - PROTON Energy Systems Inc.

- Completed and validated control board design for the HOGEN<sup>®</sup> 40 electrolyzer.
- Realized significant cost reductions on system components for the HOGEN<sup>®</sup> 40 electrolyzer through manifold components and subsystems. Prototypes were integrated into a cost reduced system and tested.
- Reduced catalyst loading for membrane and electrode assemblies; testing has shown encouraging results.

Renewable Hydrogen System Integration and Performance Modeling – Desert Research Institute

- Developed computer control of subsystems (fuel cell current, reactant flows, load bank, coolant, etc.)
- Successfully designed and implemented multiplexer to detect negative cells in the stack and removed and reapplied load as required
- Developed system control software with data logging and graphical user interface (GUI)
- Demonstrated computer control of the entire system to meet pre-planned load profile with highly variable solar and wind input

Filling up with Hydrogen 2000 – Stuart Energy Systems

- Delivered PFA Model 25 prototype to Ford Motor Company for joint evaluation field test.
- P3-1A fuel appliance prototype passed the 1000-hour time mark in SunLine Transit Field Test.
- P3-1B HP fuel appliance passed the 500-hour time mark in Powertech Field Test.

Light, Medium Duty Fleet – NRG Tech

- Finalized retrofit package design.
- Completed installation and emissions verification of retrofit packages.
- Received EPA approval.

Hydrogen Commercialization For The 21<sup>st</sup> Century - SunLine Services Group

- Expanded the SunLine project into data collection and reporting for equipment that generates and uses hydrogen in a setting of daily commercial operations and maintenance.
- Experienced exceptional interest and worldwide attention from those wanting to visit the hydrogen facilities and see /drive hydrogen vehicles.

Hydrogen and Fuel Cell Vehicle Evaluation – NREL

- Found that for significant expansion of the fuel cell bus fleet beyond a demonstration scale, substantial upgrades to fuel production, storage, and the maintenance facility at SunLine will be required.

- Determined that Codes and Standards for hydrogen need to be updated and standardized to help local fire and safety officials understand the systems.

#### Hydrogen Reformer, Fuel Cell Power Plant and Vehicle Refueling System – Air Products and Chemicals, Inc.

- Completed final performance testing and modifications to the prototype hydrogen generator for field operation in Las Vegas.
- Completed final design, assembly and performance testing of the 50kW PEM FCS.
- Completed design of the scaled-up hydrogen generator unit. Construction was initiated.

#### Hydrogen Composite Tank Program – Quantum

- Identified several limitations on choices of metallic hardware material selection due to hydrogen embrittlement, major stresses imposed by high pressure and corrosion, and automotive environmental requirements. Decisions about metallic hardware to employ were made on the basis of these findings.
- Optimized the thermoplastic liners of hydrogen storage tanks by identifying and adjusting for the limitations imposed in material selection and design due to high and low temperature performance requirements, permeation resistance and processability.
- Improved the composite shell efficiency of the hydrogen storage tanks by (1) adapting higher strength reinforcing fiber (2) improving the resin impregnation system that maximizes the translation efficiency of the fiber (3) and employing a toughened epoxy system to improve damage tolerance of the composite shell in spite of the reduced wall thickness.

#### Insulated Pressure Vessels For Vehicular Hydrogen Storage - Lawrence Livermore National Laboratory (LLNL)

- Successfully tested the insulated pressure vessels according to the DOT/ISO standards. Cycling,
- Completed a finite element analysis of the insulated pressure vessels. The results show that the vessel is subjected to plastic deformation only during the first few (5) cryogenic cycles. Additional cryogenic and high-pressure cycles do not produce plastic deformation. The analysis predicts that the vessel does not fail under repeated cryogenic and pressure cycles.
- Created a team with Structural Composites Industries (SCI) and SunLine Transit to install insulated pressure vessels into two SunLine vehicles.

#### Mine Locomotive and Loader Projects - Sandia National Laboratories

- Completed the first fuel cell powered locomotive.
- Completed the first fuel cell powered vehicle for heavy duty underground applications.

### **4.2.5 Analysis and Technology Transfer**

#### Process Analysis of Hydrogen Research Activities – NREL

- Determined cost goals for the economic feasibility of a reversible hydrogen fuel cell. Identified opportunities for using such a unit to level wind energy.

- Determined the likely cost of hydrogen from biomass via three thermochemical routes. Identified research goals for hydrogen from biomass pyrolysis.
- Identified the R&D success path required for hydrogen from algal water splitting to be economic.
- Confirmed that wind/electrolysis is a clean method of producing hydrogen, even on a life cycle basis. Identified areas of process that contribute the most to the total environmental impact.
- Found thermocatalytic decomposition of natural gas to be a viable option for producing hydrogen with fewer CO<sub>2</sub> emissions.

#### Distributed Hydrogen Fueling systems Analysis – Directed Technologies, Inc.

- Determined that a distributed hydrogen infrastructure based on steam reforming of natural gas at the local fueling station is projected to cost approximately 50% less than the cost of maintaining the existing crude oil/gasoline infrastructure. It is approximately \$600-\$800 per new fuel cell car sold for the natural gas/hydrogen infrastructure and about \$1230 per new conventional car sold for the existing infrastructure.
- Determined that by installing a 200-kW stationary fuel cell at a hydrogen fueling station designed to support 500 FCVs, and investor could make a 10% real, after-tax return on investment by selling electricity for 6¢/kWh during six on-peak hours and selling hydrogen at \$1/gallon of gasoline-equivalent. If only 100 FCVs were refueling at this station, then the on-peak electricity could be sold at 18¢/kWh and the hydrogen at \$1.50/gallon-equivalent.

#### Hydrogen Technical Analysis – Arthur D. Little

- Preliminary findings modeling a high-pressure steam reformer indicate that the use of fluorinated metal hydrides in slurry form could provide significant benefits in terms of off-board system efficiency, especially if the slurry could also be used for on-board storage.
- Determined that if non-palladium metal membranes could be further developed to operate with reasonable fluxes and at higher pressures, they could provide a very competitive alternative to PSA-based separation and purification systems, though they would not likely yield significant improvements in efficiency.

#### Inventory and Gap Analysis of Federally Funded Hydrogen R&D – NREL

- Performed a comprehensive search of the RaDiUS database. The USDA's Current Research Information Search (CRIS) was also searched to identify any missed records and obtain more complete project descriptions. Finally, DOE records were refined using available information from the Offices of Industrial Technologies, Power Technology and Science. The searches identified a total of 440 records of that are directly or relevant hydrogen energy R&D projects.
- Identified several funding gaps in the FY1999 portfolio. In the production area, it was found that thermal routes (primarily using fossil feedstocks) received four times as much funding as other possible production routes. Very little funding was directed towards purification technologies, and then only for membranes development. Metal hydrides dominated the funding for storage options, although the DOE had a fairly broad portfolio of technologies that they were supporting. Overall, storage receives less than a third of the funding that was directed towards production. Fuel cells dominated the support for utilization technologies, receiving more than \$70 million. No records were found for R&D on industrial uses of hydrogen. The DOE was the primary funding source for infrastructure work, with refueling receiving the greatest emphasis. Testing and certification was a notable gap in these efforts.

Hydrogen Infrastructure Coordination – NREL

- Initiated working with the National Fire Protection Association (NFPA) to coordinate codes and standards activities, share information, articulate standards-related issues and make standards validation work sponsored by NREL available to NFPA for use in their standards development. NFPA established a project to develop a building code NFPA 5000, a code development activity independent of the ICC. The NFPA effort is intended to include hydrogen
- Served as an invited member on the SAE Fuel Cells Standards Committee, Recycling Subcommittee, developing the first codes and standards document of its kind at either the national or international levels. The Subcommittee will be issuing draft recyclability guidelines for the PEM fuel cell system, including an assessment of compressed, liquid, chemical and metal hydride storage.

Hydrogen Technical Analysis on Matters Being Considered by the International Energy Agency – Longitude 122 West, Inc.

- Found the cost of hydrogen for fueling hydrogen vehicles to be similar for a fully utilized station, regardless of the source of hydrogen: delivered liquid, pipeline gas, or on-site production from natural gas or by electrolysis.
- Found that station footprints are dominated by the keep-out safety zone for stored hydrogen, especially liquid.
- Found hydrogen-fueled vehicles have an advantage in fuel economy and emissions over alternative vehicles, such as on-board reforming, battery hybrids and advanced ICE vehicles.

Technical Analysis of Currently Funded Projects and Outreach Activities – Energetics, Incorporated

- Performed site-visit evaluations of thirteen hydrogen projects.
- Developed databases of hydrogen stakeholders and of domestic and international hydrogen storage activities.

Strategic Planning and Implementation – NREL

- Conducted the second HTAP Scenario Planning Workshop in November 2000 in conjunction with the HTAP Fall meeting at Sunline Transit in Thousand Palms, CA. The participants developed focused scenarios to achieve the HTAP vision and trajectory-based scenarios that describe how policy and R&D initiatives might be used to move from the present situation toward the end-state scenarios encompassing the HTAP vision.

Developing a Partnership with Government and Industry to Accelerate the Commercialization of Hydrogen – National Hydrogen Association

- Held the Codes and Standards NHA workshop on March 5, 2001 in Washington, DC. The proceedings were delivered at the end of May.
- Had final editorial changes approved for circulation of the Draft Public Available Specification for WI 15916 Basic Considerations for the Safety of Hydrogen Systems. This document was circulated to the P-members of ISO-TC-197 through May 20, 2001.
- Participated in the first full meeting of the U.S. TAG members of IEC-TC-105 on March 13, 2001, in Lake Buena Vista, Florida.

## 4.3 Publications and Presentations

### 4.3.1 Production

#### Thermal Dissociation of Methane Using a Solar-Coupled Aerosol Flow Reactor – NREL

Alan W. Weimer, Jaimee Dahl, and Joseph Tamburini, Allan Lewandowski, Roland Pitts, Carl Bingham, and Gregory C. Glatzmaier, “Thermal Dissociation of Methane Using a Solar Coupled Aerosol Flow Reactor”, Proceedings of the 2000 U.S DOE Hydrogen Program Review, May 9-11, 2000, San Ramon, CA, November 2000, NREL/CP-570-28890;

Dahl, J., J. Tamburini, A. Weimer,, A. Lewandowski, J. Pitts, , C. Bingham, and G. Glatzmaier, “Thermal Dissociation of Methane Using a Solar Coupled Aerosol Flow Reactor” Proceedings of the AIChE 2000 Annual Meeting, November 12-17, 2000, Los Angeles, CA.

Dahl, J.K. et al., “Solar-thermal Processing of Methane to Produce Hydrogen and Syngas,” submitted for publication to Energy and Fuels.

Dahl, J.K. et al., “Intrinsic Kinetics for Rapid Decomposition of Methane in an Aerosol Flow Reactor,” paper submitted for publication to International Journal of Hydrogen Energy.

J. Dahl, A.W. Weimer, A. Lewandowski, R. Pitts, C. Bingham, G. Glatzmaier, “Hydrogen synthesis by the solar-thermal dissociation of methane”, 221st ACS National Meeting April 1- 5, 2001, San Diego, CA.

#### Production of H<sub>2</sub> by Superadiabatic Decomposition of Hydrogen Sulfide - Gas Technology Institute (GTI)

J. Abbasian and F. S. Lau, “Production of H<sub>2</sub> by Superadiabatic Decomposition of Hydrogen Sulfide,” Proceedings of the 2000 U.S. DOE Hydrogen Review Program review, (2000).

Rachid Slimane and F.S. Lau, “Production of H<sub>2</sub> by Superadiabatic Decomposition of Hydrogen Sulfide,” presented at the 2001 U.S. DOE Hydrogen Review Program review meeting in Baltimore.

#### Thermocatalytic CO<sub>2</sub>-free Production of Hydrogen from Hydrocarbon Fuels - Florida Solar Energy Center

Muradov, N. “Catalysis of Methane Decomposition over Elemental Carbon”, *Catalysis Communications*, vol. 2/3-4, p.89-94, 2001.

Muradov, N. “Hydrogen from Fossil Fuels without CO<sub>2</sub> Emissions”, *Advances in Hydrogen Energy*, Ed. C.Gregoire Padro and F.Lau, Kluwer Academic/Plenum Publishers, 1-16, 2000.

Muradov, N. “Thermocatalytic Production of Hydrogen via Pyrolysis of Hydrocarbon Fuels: from Methane to Residual Oil”, *Energy for 21<sup>st</sup> Century: Hydrogen Energy, Symposium, American Chemical Society Meeting*, San Diego, CA, 2001.

Muradov, N. “Hydrogen via Methane Decomposition: an Application to Decarbonization of Fossil Fuels”, *International Journal of Hydrogen Energy*, ms.# 1246, 2001.



Muradov, N. "Hydrocarbon-based Systems for CO<sub>2</sub>-free Production of Hydrogen, 13<sup>th</sup> World Hydrogen Energy Conference, Beijing, China, 2000.

Muradov, N. "Role of Hydrogen in Decarbonization of Fossil Fuels. Hydrogen from Hydrocarbons without CO<sub>2</sub> Emissions", *Forum on Converting to Hydrogen Economy*", Fort Collins, CO, 2000.

Muradov, N. "Thermocatalytic CO<sub>2</sub>-free Production of Hydrogen from Hydrocarbon Fuels", *Proc. DOE Annual Hydrogen Program Review Meeting*, San Ramon, CA, 2000.

Muradov, N. "Miniature Hydrogen Generator for Fuel Cell Applications", *Proc. DOD DARPA Palm Power Workshop*, Fort Lauderdale, FL, 2000.

Muradov, N. "Thermocatalytic CO<sub>2</sub>-free Production of Hydrogen from Hydrocarbon Fuels", *DOE Annual Hydrogen Program Review Meeting*, Baltimore, MD, 2001.

Novel Catalytic Fuel Reforming – InnovaTek, Inc.

Quentin Ming, Lloyd Allen, Todd Healey, Patricia Irving, and William J. Thomson "DEVELOPMENT OF SULFUR TOLERANT CATALYSTS FOR STEAM REFORMING OF GASOLINE AND DIESEL FUELS" Proceedings of the 222<sup>nd</sup> ACS National Meeting, Chicago, August 2001.

Qimin Ming, Todd Healey, Lloyd Allen, and Patricia Irving, "STEAM REFORMING OF HYDROCARBON FUELS" *Catalysis Today*, 2002, in press.

Irving, P.M., W. L. Allen, T. Healey, W.J. Thomson, "CATALYTIC MICRO REACTOR SYSTEMS FOR HYDROGEN GENERATION", invited presentation at the 5<sup>th</sup> International Conference on Microreaction Technology, Strasbourg, May 2001.

Irving, Patricia M., W. Lloyd Allen, Quentin Ming, and Todd H. Healey, "THE H2GEN<sup>TM</sup> GASOLINE/DIESEL PROCESSOR FOR PORTABLE FUEL CELL HYDROGEN PRODUCTION." In: Proceedings of the 2001 Conference on Small Fuel Cells, Washington DC, sponsored by The Knowledge Foundation, Brookline MA, April 2001.

Engineering Development of Ceramic Membrane Reactor Systems for Converting Natural Gas to Hydrogen and Synthesis Gas for Liquid Transportation Fuels – Air Products and Chemicals, Inc.

Gas-to-Liquids Conference, IBC, London, February 2000, P.N.Dyer and C.M.Chen, "ITM Technology for GTL Processing".

US DOE H<sub>2</sub> R&D Annual Program Review, San Ramon, CA, May 2000, P.N.Dyer and C.M.Chen, "Engineering Development of Ceramic Membrane reactor Systems for Converting Natural Gas to H<sub>2</sub> and Syngas for Liquid Transportation Fuels".

US DOE H<sub>2</sub> R&D Annual Program Review, Baltimore, MD, April 2001, P.N.Dyer and C.M.Chen, "Engineering Development of Ceramic Membrane reactor Systems for Converting Natural Gas to H<sub>2</sub> and Syngas for Liquid Transportation Fuels".

6<sup>th</sup> Natural Gas Conversion Symposium, Girdwood, Alaska, June 2001, C.M. Chen, P.N. Dyer, K.F. Gerdes, C.M. Lowe, S.R. Akhave, D.R. Rowley, K.I. Åsen and E.H. Eriksen, "An Integrated ITM Syngas/Fischer-Tropsch Process for GTL Conversion".

6<sup>th</sup> Natural Gas Conversion Symposium, Girdwood, Alaska, June 2001, M.F. Carolan, P.N. Dyer, E. Minford, T.F. Barton, D.R. Peterson, A.F. Sammells, D.L. Butt, R.A. Cutler and D.M. Taylor, "Development of the High Pressure ITM Syngas Process".

Ultra-Clean Transportation Fuels Symposium, American Chemical Society National Meeting, Chicago, IL, August 2001, C.M. Chen and P.N. Dyer, "Development of the ITM Syngas Process for GTL Conversion".

#### Supercritical Water Partial Oxidation – General Atomics

Johanson, N.W., M.H. Spritzer, G.T. Hong, W.S. Rickman. 2001. "Supercritical Water Partial Oxidation." NREL/CP-570-30535. Proceedings of the 2001 DOE Hydrogen Program Review.

"Supercritical Water Oxidation and Gasification Power Cycles – an Update on Development Progress at General Atomics." Presented at the 26<sup>th</sup> International Technical Conference on Coal utilization & Fuel Systems, March 5-8, 2001.

#### Biohydrogen Production from Renewable Organic Wastes – Iowa State University

Van Ginkel, S., Lay, J.J., and Sung, S., (2000) Biohydrogen Production Optimization Using Variable Natural Inocula. *Proceedings of Water Environment Federation 73rd Annual Conference*, Anaheim, CA.

Van Ginkel, S., Sung, S., and Lay, J.J., (2001) Biohydrogen Production as a function of pH and Substrate Concentration. *Environmental Science & Technology Journal* in Press.

Van Ginkel, S., Sung, S., Li, L., and Lay, J.J., Role of Initial Sucrose and pH Levels on Natural, Hydrogen-producing, Anaerobe Germination. Submitted to *Environmental Science & Technology Journal* for publication.

#### Bio-production of Hydrogen using Thermophilic Bacteria - NETL

"Bio-hydrogen production by the thermophilic bacterium *Thermotoga neapolitana*." Accepted for publication in the peer-reviewed journal *Applied Biochemistry and Biotechnology*. Material also presented orally and as a poster at the 23rd Annual Biofuels Meeting.

*Thermotoga neapolitana*: A microaerophile producing hydrogen in the presence of oxygen." accepted, oral presentation, 5th Biomass Conference of the Americas in Orlando, FL Sept 19, 2001.

"Hydrogen production and the order *Thermotogales*." to be presented September at IEA Annex 15/ COST Action 841 meeting in Szeged Hungary September 5-13, 2001.

#### Hydrogen from Post-consumer Wastes – NREL

Czernik, S., French, R., Feik, C., and Chornet, E.; Production of Hydrogen from Biomass by Pyrolysis/Steam Reforming, in *Advances in Hydrogen Energy*, Grégoire-Padró, C. and Lau, F., Eds., Kluwer Academic/Plenum Publishers, New York 2000, pp. 87-91.

Feik, C., French, R., Czernik, S., and Chornet, E.; Production of Hydrogen from Biomass-Derived Liquids, in *ASME Proceedings of the Solar Engineering 2000 Conference*; Madison, Wisconsin; June 16-21, 2000; Eds. Pacheco, J.E. and Thornbloom, M. D.; pp. 175 – 179.

Czernik, S., French, R., Feik, C., Chornet, E.; Hydrogen from Biomass-Derived liquids, in *Progress in Biomass Thermochemical Conversion* (in press).

Biological Hydrogen from Fuel Gases and from Water – NREL

Maness, P.C. and P.F. Weaver. 2001. "Evidence for three distinct hydrogenase activities in *Rhodospirillum rubrum*." Submitted to Applied Microbiology and Biotechnology.

Bioreactor Development For Biological H<sub>2</sub> Production – NREL

Manuscript entitled "Bioreactor Design Studies for a Novel Hydrogen-Producing Bacterium", E. Wolfrum, A. Watt, accepted for publication in Applied Biochemistry and Biotechnology (2001)

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#### Hydrogen Technical Analysis – Arthur D. Little

As this program is focused on the analysis of technologies, we do not expect to develop patentable intellectual property. Our *Hydrogen Technical Analysis* paper is available in the Proceedings of the 2001 U.S. DOE Hydrogen Program Review.

#### Inventory and Gap Analysis of Federally Funded Hydrogen R&D – NREL

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#### Hydrogen Infrastructure Coordination – NREL

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Hydrogen Technical Analysis on Matters Being Considered by the International Energy Agency – Longitude 122 West, Inc.

S. Schoenung, “Hydrogen Vehicle Refueling Infrastructure Alternatives: An Analysis Developed for the International Energy Agency,” Proc. 11<sup>th</sup> Canadian Hydrogen Conference, Victoria, Canada, June 2001

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Strategic Planning and Implementation – NREL

A draft report was prepared summarizing the results of Workshop II and distributed to all participants

Presentation on HTAP scenario planning at National Hydrogen Association meeting in March 2001

Article on HTAP scenario planning for NHA newsletter

Lecture on hydrogen energy and fuels cells for Graduate Engineering Seminar series, Colorado State University

Presentation on renewable hydrogen energy and fuel cells to the Delta-Montrose Electric Association

Interviews with reporters from *Business Week*, *CNN*, *USA Today*, and other publications on hydrogen energy

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